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Origin invariance in vibrational resonance Raman optical activity

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A theoretical investigation on the origin dependence of the vibronic polarizabilities, isotropic and anisotropic rotational invariants, and scattering cross sections in Resonance Raman Optical Activity (RROA) spectroscopy is presented. Expressions showing the origin dependence of these polarizabilities were written in the resonance regime using the Franck-Condon (FC) and Herzberg-Teller (HT) approximations for the electronic transition moments. Differently from the far-from-resonance scattering regime, where the origin dependent terms cancel out when the rotational invariants are calculated, RROA spectrum can exhibit some origin dependence even for eigenfunctions of the electronic Hamiltonian. At the FC level, the RROA spectrum is completely origin invariant if the polarizabilities are calculated using a single excited state or for a set of degenerate states. Otherwise, some origin effects can be observed in the spectrum. At the HT level, RROA spectrum is origin dependent even when the polarizabilities are evaluated from a single excited state but the origin effect is expected to be small in this case. Numerical calculations performed for (S)-methyloxirane, (2R,3R)-dimethyloxirane, and (R)-4-F-2-azetidinone at both FC and HT levels using the velocity representation of the electric dipole and quadrupole transition moments confirm the predictions of the theory and show the extent of origin effects and the effectiveness of suggested ways to remove them. [http://dx.doi.org/10.1063/1.4918935]

I. INTRODUCTION

In the last decades, Quantum-Mechanical (QM) methods have been developed and implemented in many computational packages for the calculation of various chiroptical properties and spectroscopies, such as Optical Rotation (OR), Electronic Circular Dichroism (ECD), and Vibrational Optical Activity (VOA), comprising Vibrational Circular Dichroism (VCD) and non-resonant vibrational Raman Optical Activity (ROA).[1–6] The latter techniques have gained increasing interest recently as valuable tools for assigning the absolute configurations and for obtaining information on the local environment of oscillating modes of molecular systems and on conformational ratios important in determining reactivities of biomolecules.[5,7] The tremendous progress of *ab initio* quantum chemistry in such a field has been reflected in the larger number of applications of QM approaches to the calculation of chiroptical properties and spectroscopies.[5,7–11] Especially in the field of VOA, the impact of QM methods has been so large that, in 2007, Polavarapu[12] has talked of a renaissance in chiroptical methods due to the accuracy and computational efficiency achieved by *ab initio* QM methods in reproducing experimental data and predicting new ones. Most of these studies are based on response methods within the density functional theory (DFT) or time-dependent DFT (TD-DFT) even if more accurate methods such as coupled cluster have also been used.[13,14] In general, the results that can nowadays be achieved in such a field are so reliable and accurate that QM protocols have become a powerful methodology to assist experimentalists in the reliable determination of the molecular absolute configuration.[15]

One of the recognized shortcomings of VOA is the weakness of the signal, which in some cases prevents the experimental study of complex molecular systems or the investigation of some specific spectral regions. Besides the improvement of instruments which has been reported in recent years,[5] strategies for enhancing the VOA signal have been identified, spanning the field of the creation of supramolecular structures,[16–18] interaction with metal nanoparticles,[19,20] and especially taking advantage of resonance effects.[21–23] In the particular case of ROA, experiments performed in the resonance regime, which give rise to the so-called Resonance Raman Optical Activity (RROA),[24,25] have been reported to yield a huge increase in the ROA signal. Nevertheless, the potentialities of RROA remain to date almost unexplored, and only a few measurements have been reported in the literature.[21–23] One possible cause of this situation may be the scarcity of computational approaches to calculate RROA spectra currently available,[26,27] which makes the interpretation of the signals and the assignment of the spectra difficult.

In line with previous work of some of the present authors,[28–33] we aim to develop accurate yet user-friendly strategies for the calculation of RROA spectra of complex systems, also interacting with external complex environments. Here, we start our investigation on such a field, by addressing the problem of origin invariance in RROA, a fundamental

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topic which, to the best our knowledge, has never been directly addressed. In the following, a purely theoretical derivation of the equations demonstrating the problem of the dependence of ROA vibronic polarizabilities and rotational invariants is reported, just after a brief recalling of the fundamental theory underlying RROA. Then, the numerical evaluation of the extent of the effect, and of the effectiveness of the proposed strategies to overcome the problem, is reported with special reference to the calculation of RROA spectra of (S)-Methyloxirane, (2R,3R)-dimethyloxirane, and (R)-4-F-2-azetidinone. Some conclusions and the discussion of the perspectives of this work end the manuscript.

II. GENERAL VIBRONIC ROA THEORY

In this section, we will briefly recall the fundamental theory of circularly polarized (CP) Raman optical activity.[5,24,25,34] In the Raman effect, the intensity of the scattered radiation depends on the polarization conditions of the incident and observed light beams, the angle ξ between them, the temperature of the sample and its characteristics (e.g., concentration and physical state), and the fourth power of the excitation angular frequency ω_0. The molecular contribution to the light scattering is given by the polarizability tensor, $\boldsymbol{\alpha}$, which itself is function of ω_0. The intensities are usually expressed in terms of cross sections. For instance, the scattered CP Raman differential cross section with $\xi = 180°$ (backscattering) and unpolarized incident light is[5]

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{Raman}} = 4K\left[45\alpha^2 + 7\beta_S(\alpha)^2 + 5\beta_A(\alpha)^2\right], \quad (1)$$

where

$$K = \left(\frac{\pi}{\epsilon_0}\right)^2\left(\frac{\omega_R}{2\pi c}\right)^4\frac{N_i}{90}, \quad (2)$$

and ϵ_0 is the vacuum electric permittivity, c is the speed of light, N_i is the number density of molecules in the initial state i, at some temperature T, and ω_R is the angular frequency of the Raman scattering. The terms α^2, $\beta_S(\alpha)^2$, and $\beta_A(\alpha)^2$ are the *isotropic*, *symmetric anisotropic*, and *anti-symmetric anisotropic* rotational invariants of $\boldsymbol{\alpha}$.[5,34] If the polarization states of the incident and/or scattered radiation are specified to be of circular type and the difference in Raman intensity for right minus left circularly polarized light is measured, one obtains a CP Raman optical activity spectrum. By selecting the polarization states of the incident and observed light between linear and circular, four different forms of CP ROA are possible: (1) Incident Circular Polarization (ICP) ROA, (2) Scattered Circular Polarization (SCP) ROA, (3) in-phase Dual Circular Polarization (DCP_I) ROA and (4) out-of-phase Dual Circular Polarization (DCP_II) ROA.[5] The corresponding SCP ROA differential cross section is given by the following combination of ten ROA invariants:[5]

$$\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_{\text{ROA}} = \frac{8K}{c}\big[&-45\alpha G + 5\beta_S(G)^2 - 5\beta_A(G)^2 \\ &+ 3\beta_S(A)^2 + \beta_A(A)^2 - 45\alpha\mathcal{G} - 7\beta_S(\mathcal{G})^2 \\ &- 5\beta_A(\mathcal{G})^2 + \beta_S(\mathcal{A})^2 + \beta_A(\mathcal{A})^2\big]. \end{aligned} \quad (3)$$

These rotational invariants are built from products between $\boldsymbol{\alpha}$ and any of the four ROA tensors: (i) $\boldsymbol{G}$, the electric dipole-magnetic dipole polarizability tensor, (ii) $\boldsymbol{\mathcal{G}}$, the magnetic dipole-electric dipole tensor, (iii) $\boldsymbol{A}$, the electric dipole-electric quadrupole tensor, and (iv) $\boldsymbol{\mathcal{A}}$, the electric quadrupole-electric dipole tensor,[5,34]

$$\alpha G = \frac{1}{9}\Im\left[(\alpha_{\alpha\alpha})^S(G_{\beta\beta})^{S*}\right] \quad (4)$$

$$\beta_S(G)^2 = \frac{1}{2}\Im\left[3(\alpha_{\alpha\beta})^S(G_{\alpha\beta})^{S*} - (\alpha_{\alpha\alpha})^S(G_{\beta\beta})^{S*}\right] \quad (5)$$

$$\beta_A(G)^2 = \frac{3}{2}\Im\left[(\alpha_{\alpha\beta})^A(G_{\alpha\beta})^{A*}\right] \quad (6)$$

$$\beta_S(A)^2 = \frac{1}{2}\omega_0\Im\left\{i(\alpha_{\alpha\beta})^S\left[\epsilon_{\alpha\gamma\delta}(A_{\gamma,\delta\beta})\right]^{S*}\right\} \quad (7)$$

$$\begin{aligned}\beta_A(A)^2 = \frac{1}{2}\omega_0\Im\Big\{&i(\alpha_{\alpha\beta})^A\left\{\left[\epsilon_{\alpha\gamma\delta}(A_{\gamma,\delta\beta})\right]^{A*}\right. \\ &\left.+\left[\epsilon_{\alpha\beta\gamma}(A_{\delta,\gamma\delta})\right]^{A*}\right\}\Big\}, \end{aligned} \quad (8)$$

and the other five are associated with the script font tensors. They have the same mathematical form of invariants (4)–(8) but the angular frequency of scattered light ω_R replaces ω_0 in the expressions for $\beta_S(\mathcal{A})^2$ and $\beta_A(\mathcal{A})^2$ invariants. The superscripts S and A mean the symmetric and anti-symmetric forms of the tensor. $\boldsymbol{\epsilon}$ is the third-rank anti-symmetric unit tensor and the Einstein summation convention over repeated greek subscripts is adopted above and throughout this work.

A. Franck-Condon (FC) and Herzberg-Teller (HT) approximations

In order to evaluate Raman and ROA tensors, the electronic transition moments must be written as a function of vibrational coordinates. This can be achieved by expanding them in a Taylor series of, for instance, the normal coordinates of the ground electronic state,[35,36]

$$\langle e_g|\hat{o}_a|e_r\rangle = o^{gr}_{a,0} + \sum_k o^{gr}_{a,k}Q^g_k + \frac{1}{2}\sum_k\sum_l o^{gr}_{a,kl}Q^g_kQ^g_l + \cdots, \quad (9)$$

where $\langle e_g|\hat{o}_a|e_r\rangle$ is a transition moment between the ground, e_g, and excited state, e_r, of the operator $\hat{o}_a$, which represents a Cartesian component of the electric dipole, magnetic dipole or electric quadrupole operators. In Eq. (9), $o^{gr}_{a,0}$, $o^{gr}_{a,k}$, and $o^{gr}_{a,kl}$ correspond to $\langle e_g|\hat{o}_a|e_r\rangle$ and its first and second derivatives, respectively, evaluated at the equilibrium ground state geometry. The simplest level of approximation is to assume that the transition takes place in such a short time that the position of the nuclei remains almost unchanged and the transition dipoles can be considered as constant. This is known as the FC principle and corresponds to a truncation of expansion (9) at the zeroth order term $o^{gr}_{a,0}$. An extension to the FC principle was proposed by Herzberg and Teller:[37] in this case, it accounts for a linear variation of the transition moment with respect to the normal coordinates, i.e., the first order terms $o^{gr}_{a,k}$ of Eq. (9) are considered. At the HT level, any

of the five Raman/ROA tensors related to the resonance scattering have the general form given as[5,36]

$$T_{ab} = \frac{1}{\hbar}\sum_{\{e_r\}}\left(\sum_{n}\frac{o^{gr}_{a,0}o^{rg}_{b,0}\langle f^g|n^r\rangle\langle n^r|i^g\rangle}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}} + \sum_{n,k}\frac{o^{gr}_{a,k}o^{rg}_{b,0}\langle f^g|Q^g_k|n^r\rangle\langle n^r|i^g\rangle}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}}\right.$$
$$\left. + \sum_{n,k}\frac{o^{gr}_{a,0}o^{rg}_{b,k}\langle f^g|n^r\rangle\langle n^r|Q^g_k|i^g\rangle}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}} + \sum_{n,k,l}\frac{o^{gr}_{a,k}o^{rg}_{b,l}\langle f^g|Q^g_k|n^r\rangle\langle n^r|Q^g_l|i^g\rangle}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}}\right), \quad (10)$$

where $|i^g\rangle$ and $|f^g\rangle$ are the initial and final vibrational wavefunctions of the ground e_g and $|n^r\rangle$ is an intermediate vibrational wavefunction of the excited state e_r. The denominators $\omega_{rg} = (E_{e_r} - E_{e_g})/\hbar$ and $\omega_{ni} = (E_{n^r} - E_{i^g})/\hbar$ are energy differences between electronic and vibrational states, respectively. The Γ_{e_r} term is related to the lifetime of the excited state e_r and is assumed to be independent of the vibrational state n^r. The electronic states between brackets in Eq. (10), $\{e_r\}$, are those in resonance with the incident radiation, while n represents an intermediate vibrational state. The first fraction on the right-hand side of Eq. (10), containing the zeroth order terms $o^{gr}_{a,0}$ and $o^{rg}_{b,0}$, corresponds to the FC approximation for the general Raman/ROA tensor $\boldsymbol{T}$. The other three terms account for HT effects.

B. Origin dependence

In this section, we investigate the origin dependence of the ROA tensors evaluated within the FC and HT approximations and the requirements to ensure origin invariance for the ten ROA rotational invariants in Eq. (3). Both FC and HT levels demand the calculation of electronic transition moments for the electric dipole, magnetic dipole, and electric quadrupole operators, and in addition, the HT level requires their geometric derivatives. Hartree atomic units are used throughout this section and subsections. Starting with the electric dipole transition moment, when the origin is shifted from $\boldsymbol{O}$ to $\boldsymbol{O}+\boldsymbol{a}$, we have[38]

$$\begin{aligned}\mu^{gs}_\alpha(\boldsymbol{O}+\boldsymbol{a}) &= -\left\langle e_g\left|\sum_j(\boldsymbol{r}_j-\boldsymbol{a})_\alpha\right|e_r\right\rangle \\ &= -\left\langle e_g\left|\sum_j(\boldsymbol{r}_j)_\alpha\right|e_r\right\rangle + \langle e_g|e_r\rangle\left(\sum_j(\boldsymbol{a})_\alpha\right) \\ &= \mu^{gs}_\alpha(\boldsymbol{O}), \end{aligned} \quad (11)$$

where e_g and e_r are two different electronic states and $(\boldsymbol{r}_j)_\alpha$ is the α-component of the position vector for electron j. Nuclear charges cannot contribute to $\boldsymbol{\mu}^{gs}$ and the corresponding term was omitted from the electric dipole operator in Eq. (11). For the same reason, nuclear terms will be omitted in those expressions concerning the magnetic dipole and electric quadrupole transition moments. The HT linear expansion of Eq. (11) is given by

$$\begin{aligned}\mu^{gr}_\alpha(\boldsymbol{O}+\boldsymbol{a}) &= \mu^{gr}_{\alpha,0}(\boldsymbol{O}+\boldsymbol{a}) + \sum_k \mu^{gr}_{\alpha,k}(\boldsymbol{O}+\boldsymbol{a})Q^g_k \\ &= \mu^{gr}_{\alpha,0}(\boldsymbol{O}+\boldsymbol{a}) + \sum_k\left(\frac{\partial\mu^{gr}_\alpha(\boldsymbol{O}+\boldsymbol{a})}{\partial Q^g_k}\right)_0 Q^g_k \\ &= \mu^{gr}_{\alpha,0}(\boldsymbol{O}) + \sum_k\left(\frac{\partial\mu^{gr}_\alpha(\boldsymbol{O})}{\partial Q^g_k}\right)_0 Q^g_k = \mu^{gr}_\alpha(\boldsymbol{O}). \end{aligned} \quad (12)$$

Note that in Eq. (12), the symbol μ^{gr}_α represents the α-component of the transition moment at an arbitrary geometry, while $\mu^{gr}_{\alpha,0}$ and $\mu^{gr}_{\alpha,k}$ represent this component and its first derivative at the equilibrium geometry. Evidently, the electric dipole-electric dipole polarizability is origin invariant,

$$\alpha_{\alpha\beta}(\boldsymbol{O}+\boldsymbol{a}) = \alpha_{\alpha\beta}(\boldsymbol{O}). \quad (13)$$

The magnetic dipole transition moment, on the other hand, is origin dependent,

$$\begin{aligned}m^{gs}_\alpha(\boldsymbol{O}+\boldsymbol{a}) &= -\frac{1}{2}\left\langle e_g\left|\sum_j\left((\boldsymbol{r}_j-\boldsymbol{a})\times\boldsymbol{p}_j\right)_\alpha\right|e_r\right\rangle \\ &= -\frac{1}{2}\left\langle e_g\left|\sum_j(\boldsymbol{r}_j\times\boldsymbol{p}_j)_\alpha\right|e_r\right\rangle \\ &\quad + \frac{1}{2}\left\langle e_g\left|\sum_j(\boldsymbol{a}\times\boldsymbol{p}_j)_\alpha\right|e_r\right\rangle \\ &= m^{gs}_\alpha(\boldsymbol{O}) + \frac{1}{2}\varepsilon_{\alpha\beta\gamma}a_\beta p^{gs}_\gamma, \end{aligned} \quad (14)$$

and this dependency is given by the cross product between the shift vector $\boldsymbol{a}$ and the angular momentum transition moment $\boldsymbol{p}^{gs}$. The HT expansion of $m^{gs}_\alpha(\boldsymbol{O}+\boldsymbol{a})$ is given by

$$\begin{aligned}m^{gr}_\alpha(\boldsymbol{O}+\boldsymbol{a}) &= m^{gr}_{\alpha,0}(\boldsymbol{O}+\boldsymbol{a}) + \sum_k\left(\frac{\partial m^{gr}_\alpha(\boldsymbol{O}+\boldsymbol{a})}{\partial Q^g_k}\right)_0 Q^g_k \\ &= m^{gr}_{\alpha,0}(\boldsymbol{O}) + \frac{1}{2}\varepsilon_{\alpha\beta\gamma}a_\beta p^{gr}_{\gamma,0} + \sum_k m^{gr}_{\alpha,k}(\boldsymbol{O})Q^g_k \\ &\quad + \frac{1}{2}\varepsilon_{\alpha\beta\gamma}a_\beta\sum_k p^{gr}_{\gamma,k}Q^g_k \\ &= m^{gr}_\alpha(\boldsymbol{O}) + \frac{1}{2}\varepsilon_{\alpha\beta\gamma}a_\beta\left(p^{gr}_{\gamma,0} + \sum_k p^{gr}_{\gamma,k}Q^g_k\right). \end{aligned} \quad (15)$$

For eigenfunctions of the electronic Hamiltonian and for approximate wavefunctions written using a complete basis set, the momentum and electric dipole matrix elements are

linearly dependent,[38–41]

$$p_\gamma^{gr} = -i\omega_{gr}\mu_\gamma^{gr}, \tag{16}$$

and Eq. (15) can be rewritten as

$$m_\alpha^{gr}(\boldsymbol{O}+\boldsymbol{a}) = m_\alpha^{gr}(\boldsymbol{O}) - \frac{i}{2}\varepsilon_{\alpha\beta\gamma}a_\beta\left(\omega_{gr,0}\,\mu_{\gamma,0}^{gr} + \sum_k[\omega_{gr,0}\,\mu_{\gamma,k}^{gr} + \omega_{gr,k}\,\mu_{\gamma,0}^{gr}]Q_k^g\right), \tag{17}$$

where $\omega_{gr,0} \equiv (E_g - E_r)/\hbar$ with both E_g and E_r energies being evaluated at the ground state equilibrium geometry and

$$\omega_{gr,k} \equiv \left(\frac{\partial\omega_{gr}}{\partial Q_k^g}\right)_0. \tag{18}$$

Equation (17) is valid for variational wavefunctions of finite basis sets as well, if they are built by using Gauge Including Atomic Orbitals (GIAOs).[40,42] The origin dependence of the $\boldsymbol{G}$ and $\boldsymbol{\mathcal{G}}$ tensors is conveniently expressed by defining a quantity that resembles an electric dipole-electric dipole polarizability multiplied by $\omega_{rg,0}$,

$$G_{\alpha\beta}(\boldsymbol{O}+\boldsymbol{a}) = G_{\alpha\beta}(\boldsymbol{O}) - \frac{i}{2}\varepsilon_{\beta\gamma\delta}a_\gamma\alpha_{\alpha\delta}^{\omega}, \tag{19}$$

$$\mathcal{G}_{\alpha\beta}(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{G}_{\alpha\beta}(\boldsymbol{O}) + \frac{i}{2}\varepsilon_{\alpha\gamma\delta}a_\gamma\alpha_{\delta\beta}^{\omega}, \tag{20}$$

and

$$\begin{aligned}\alpha_{\alpha\delta}^{\omega} \equiv \frac{1}{\hbar}\sum_{\{e_r\}}\sum_n \frac{\omega_{rg,0}}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}}\Big[&\mu_{\alpha,0}^{gr}\mu_{\delta,0}^{rg}\langle f^g|n^r\rangle\langle n^r|i^g\rangle\\ &+\sum_k[\mu_{\alpha,k}^{gr}+\omega_{rg,0}^{-1}\omega_{rg,k}\,\mu_{\alpha,0}^{gr}]\mu_{\delta,0}^{rg}\langle f^g|Q_k^g|n^r\rangle\langle n^r|i^g\rangle\\ &+\sum_k\mu_{\alpha,0}^{gr}[\mu_{\delta,k}^{rg}+\omega_{rg,0}^{-1}\omega_{rg,k}\mu_{\delta,0}^{rg}]\langle f^g|n^r\rangle\langle n^r|Q_k^g|i^g\rangle\\ &+\sum_{k,l}[\mu_{\alpha,k}^{gr}+\omega_{rg,0}^{-1}\omega_{rg,k}\mu_{\alpha,0}^{gr}]\,[\mu_{\delta,l}^{rg}+\omega_{rg,0}^{-1}\omega_{rg,l}\mu_{\delta,0}^{rg}]\langle f^g|Q_k^g|n^r\rangle\langle n^r|Q_l^g|i^g\rangle\Big].\end{aligned} \tag{21}$$

The traceless electric quadrupole transition moment is also origin dependent,

$$\begin{aligned}\theta_{\alpha\beta}^{gs}(\boldsymbol{O}+\boldsymbol{a}) &= \left\langle e_g\left|-\frac{1}{2}\sum_j\Big(3(\boldsymbol{r}_j-\boldsymbol{a})_\alpha(\boldsymbol{r}_j-\boldsymbol{a})_\beta - (\boldsymbol{r}_j-\boldsymbol{a})^2\delta_{\alpha\beta}\Big)\right|e_r\right\rangle\\ &= \theta_{\alpha\beta}^{gs}(\boldsymbol{O}) - \frac{3}{2}a_\alpha\mu_\beta^{gs} - \frac{3}{2}a_\beta\mu_\alpha^{gs} + a_\gamma\mu_\gamma^{gs}\delta_{\alpha\beta},\end{aligned} \tag{22}$$

and within the HT approximation, we have

$$\begin{aligned}\theta_{\alpha\beta}^{gs}(\boldsymbol{O}+\boldsymbol{a}) &= \theta_{\alpha\beta,0}^{gr}(\boldsymbol{O}+\boldsymbol{a}) + \sum_k\left(\frac{\partial\theta_{\alpha\beta}^{gr}(\boldsymbol{O}+\boldsymbol{a})}{\partial Q_k^g}\right)_0 Q_k^g\\ &= \theta_{\alpha\beta,0}^{gs}(\boldsymbol{O}) - \frac{3}{2}a_\alpha\mu_{\beta,0}^{gs} - \frac{3}{2}a_\beta\mu_{\alpha,0}^{gs} + a_\gamma\mu_{\gamma,0}^{gs}\delta_{\alpha\beta}\\ &\quad + \sum_k\left(\theta_{\alpha\beta,k}^{gr}(\boldsymbol{O}) - \frac{3}{2}a_\alpha\mu_{\beta,k}^{gs} - \frac{3}{2}a_\beta\mu_{\alpha,k}^{gs} + \delta_{\alpha\beta}a_\gamma\mu_{\gamma,k}^{gs}\right)Q_k^g\\ &= \theta_{\alpha\beta}^{gs}(\boldsymbol{O}) - \frac{3}{2}a_\alpha\left(\mu_{\beta,0}^{gs} + \sum_k\mu_{\beta,k}^{gs}Q_k^g\right) - \frac{3}{2}a_\beta\left(\mu_{\alpha,0}^{gs} + \sum_k\mu_{\alpha,k}^{gs}Q_k^g\right)\\ &\quad + \delta_{\alpha\beta}a_\gamma\left(\mu_{\gamma,0}^{gs} + \sum_k\mu_{\gamma,k}^{gs}Q_k^g\right).\end{aligned} \tag{23}$$

When the $\boldsymbol{A}$ and $\boldsymbol{\mathcal{A}}$ tensors are obtained from Eqs. (10), (12), and (23), those terms describing the origin dependence can be grouped in three polarizabilities,

$$A_{\alpha,\beta\gamma}(\boldsymbol{O}+\boldsymbol{a}) = A_{\alpha,\beta\gamma}(\boldsymbol{O}) - \frac{3}{2}a_\beta\alpha_{\alpha\gamma} - \frac{3}{2}a_\gamma\alpha_{\alpha\beta} + \delta_{\beta\gamma}a_\delta\alpha_{\alpha\delta}, \tag{24}$$

$$\mathcal{A}_{\alpha,\beta\gamma}(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{A}_{\alpha,\beta\gamma}(\boldsymbol{O}) - \frac{3}{2}a_\beta\alpha_{\gamma\alpha} - \frac{3}{2}a_\gamma\alpha_{\beta\alpha} + \delta_{\beta\gamma}a_\delta\alpha_{\delta\alpha}. \tag{25}$$

1. Velocity representation

An alternative to the use of GIAOs to achieve origin invariance for approximate wavefunctions is the adoption of *velocity representation* of the electric dipole, $(\mu_\alpha^{gr})^p$, and traceless quadrupole, $(\theta_{\alpha\beta}^{gr})^p$, transition moments,[38]

$$\mu_\alpha^{gr} = i\omega_{gr}^{-1}p_\alpha^{gr} = -i\omega_{gr}^{-1}(\mu_\alpha^{gr})^p, \tag{26}$$

$$\begin{aligned}\theta_{\alpha\beta}^{gr} &= -(i\omega_{gr})^{-1}\left\langle e_g\right| - \frac{1}{2}\sum_j 3(p_{j_\alpha}r_{j_\beta} + r_{j_\alpha}p_{j_\beta}) - (p_{j_\alpha}r_{j_\alpha} + r_{j_\alpha}p_{j_\alpha})\left|e_r\right\rangle \\ &= (i\omega_{gr})^{-1}(\theta_{\alpha\beta}^{gr})^p.\end{aligned} \tag{27}$$

The HT expansion of the above expressions are

$$-i\omega_{gr}^{-1}(\mu_\alpha^{gr})^p = -i\omega_{gr,0}^{-1}(\mu_{\alpha,0}^{gr})^p - i\omega_{gr,0}^{-2}\sum_k\left(\omega_{gr,0}(\mu_{\alpha,k}^{gr})^p - \omega_{gr,k}(\mu_{\alpha,0}^{gr})^p\right)Q_k^g, \tag{28}$$

$$(i\omega_{gr})^{-1}(\theta_{\alpha\beta}^{gr})^p = -i\omega_{gr,0}^{-1}(\theta_{\alpha\beta,0}^{gr})^p - i\omega_{gr,0}^{-2}\sum_k\left(\omega_{gr,0}(\theta_{\alpha\beta,k}^{gr})^p - \omega_{gr,k}(\theta_{\alpha\beta,0}^{gr})^p\right)Q_k^g. \tag{29}$$

In the velocity representation, similar equations are obtained for the origin shifted electric-magnetic dipole tensors,

$$G_{\alpha\beta}^p(\boldsymbol{O}+\boldsymbol{a}) = G_{\alpha\beta}^p(\boldsymbol{O}) - \frac{i}{2}\varepsilon_{\beta\gamma\delta}a_\gamma(\alpha_{\alpha\delta}^\omega)^p, \tag{30}$$

$$\mathcal{G}_{\alpha\beta}^p(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{G}_{\alpha\beta}^p(\boldsymbol{O}) + \frac{i}{2}\varepsilon_{\alpha\gamma\delta}a_\gamma(\alpha_{\delta\beta}^\omega)^p, \tag{31}$$

where

$$\begin{aligned}(\alpha_{\alpha\delta}^\omega)^p \equiv \frac{1}{\hbar}\sum_{\{e_r\}}\sum_n \frac{\omega_{rg,0}^{-1}}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}}\Big[&(\mu_{\alpha,0}^{gr})^p(\mu_{\delta,0}^{rg})^p\langle f^g|n^r\rangle\langle n^r|i^g\rangle \\ &+ \omega_{rg,0}^{-1}(\mu_{\delta,0}^{rg})^p\langle n^r|i^g\rangle\sum_k[\omega_{rg,0}(\mu_{\alpha,k}^{gr})^p - \omega_{rg,k}(\mu_{\alpha,0}^{gr})^p]\langle f^g|Q_k^g|n^r\rangle \\ &+ \omega_{rg,0}^{-1}(\mu_{\alpha,0}^{gr})^p\langle f^g|n^r\rangle\sum_k[\omega_{rg,0}(\mu_{\delta,k}^{rg})^p - \omega_{rg,k}(\mu_{\delta,0}^{rg})^p]\langle n^r|Q_k^g|i^g\rangle \\ &+ \omega_{rg,0}^{-2}\sum_{k,l}[\omega_{rg,0}(\mu_{\alpha,k}^{gr})^p - \omega_{rg,k}(\mu_{\alpha,0}^{gr})^p]\,[\omega_{rg,0}(\mu_{\delta,l}^{rg})^p - \omega_{rg,l}(\mu_{\delta,0}^{rg})^p]\,\langle f^g|Q_k^g|n^r\rangle\langle n^r|Q_l^g|i^g\rangle\Big],\end{aligned} \tag{32}$$

and $(\mu_{\alpha,0}^{gr})^p$ and $(\mu_{\alpha,k}^{gr})^p$ are the α-component of the velocity electric dipole transition moment and its first derivative evaluated at the equilibrium geometry. The velocity expressions for the origin shifted transition quadrupole and its related polarizabilities are given as

$$(\theta_{\alpha\beta}^{gr})^p(\boldsymbol{O}+\boldsymbol{a}) = (\theta_{\alpha\beta}^{gr})^p(\boldsymbol{O}) - \frac{3}{2}a_\alpha(\mu_\beta^{gr})^p - \frac{3}{2}a_\beta(\mu_\alpha^{gr})^p + \delta_{\alpha\beta}a_\gamma(\mu_\gamma^{gr})^p \tag{33}$$

and

$$A_{\alpha,\beta\gamma}^p(\boldsymbol{O}+\boldsymbol{a}) = A_{\alpha,\beta\gamma}^p(\boldsymbol{O}) - \frac{3}{2}a_\beta\alpha_{\alpha\gamma}^p - \frac{3}{2}a_\gamma\alpha_{\alpha\beta}^p + \delta_{\beta\gamma}a_\delta\alpha_{\alpha\delta}^p, \tag{34}$$

$$\mathcal{A}_{\alpha,\beta\gamma}^p(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{A}_{\alpha,\beta\gamma}^p(\boldsymbol{O}) - \frac{3}{2}a_\beta\alpha_{\gamma\alpha}^p - \frac{3}{2}a_\gamma\alpha_{\beta\alpha}^p + \delta_{\beta\gamma}a_\delta\alpha_{\delta\alpha}^p. \tag{35}$$

The five Raman and ROA velocity tensors appearing in the above equations are obtained when the right-hand side of Eqs. (28) and (29) replaces the electric dipole and quadrupole transition moments in Eq. (10). For instance, the velocity polarizability $\alpha_{\alpha\beta}^p$

is given by

$$\alpha^{p}_{\alpha\beta} = \frac{1}{\hbar}\sum_{\{e_r\}}\sum_{n}\frac{\omega^{-2}_{rg,0}}{\omega_{rg}+\omega_{ni}-\omega_0-i\Gamma_{e_r}}\Big[(\mu^{gr}_{\alpha,0})^p(\mu^{rg}_{\beta,0})^p\langle f^g|n^r\rangle\langle n^r|i^g\rangle$$
$$+\omega^{-1}_{rg}(\mu^{rg}_{\beta,0})^p\langle n^r|i^g\rangle\sum_k[\omega_{rg,0}(\mu^{gr}_{\alpha,k})^p-\omega_{rg,k}(\mu^{gr}_{\alpha,0})^p]\langle f^g|Q^g_k|n^r\rangle$$
$$+\omega^{-1}_{rg}(\mu^{gr}_{\alpha,0})^p\langle f^g|n^r\rangle\sum_k[\omega_{rg,0}(\mu^{rg}_{\beta,k})^p-\omega_{rg,k}(\mu^{rg}_{\beta,0})^p]\langle n^r|Q^g_k|i^g\rangle$$
$$+\omega^{-2}_{rg,0}\sum_{k,l}[\omega_{rg,0}(\mu^{gr}_{\alpha,k})^p-\omega_{rg,k}(\mu^{gr}_{\alpha,k})^p][\omega_{rg,0}(\mu^{rg}_{\beta,l})^p-\omega_{rg,l}(\mu^{rg}_{\beta,0})^p]\langle f^g|Q^g_k|n^r\rangle\langle n^r|Q^g_l|i^g\rangle\Big]. \quad (36)$$

In Secs. II B 2–II B 4, the length representation of the ten rotational invariants of ROA is assumed to establish the necessary conditions for their origin invariance. However, since length and velocity equations expressing the origin dependence of the resonance ROA tensors are mathematically identical, the same conclusions apply to the velocity forms of these rotational invariants.

2. The αG and αG invariants

The origin dependence of αG arises from $G^{S*}_{\beta\beta}$ as follows:

$$\big(G_{\beta\beta}(\boldsymbol{O}+\boldsymbol{a})\big)^{S*} = \left[\big(G_{\beta\beta}(\boldsymbol{O})\big)^{S} - \frac{ia_\gamma}{2}\varepsilon_{\beta\gamma\delta}\alpha^{\omega}_{\beta\delta}\right]^{*}. \quad (37)$$

The second term on the right-hand side of Eq. (37),

$$-\frac{ia_\gamma}{2}\varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\beta\delta} = -\frac{i}{2}\alpha^{\omega*}_{\beta\delta}(a_x\varepsilon_{\beta x\delta}+a_y\varepsilon_{\beta y\delta}+a_z\varepsilon_{\beta z\delta}), \quad (38)$$

contains the components a_γ of the shift vector which are arbitrary quantities. Therefore, in order to make Eq. (38) equal to zero, the terms containing the same component of $\boldsymbol{a}$ must cancel each other. After summing over β and δ indexes, one obtains the following three independent equations:

$$\frac{i}{2}a_x\varepsilon_{\beta x\delta}\alpha^{\omega*}_{\beta\delta} = \frac{i}{2}a_x(\alpha^{\omega*}_{zy}-\alpha^{\omega*}_{yz}), \quad (39)$$
$$\frac{i}{2}a_y\varepsilon_{\beta y\delta}\alpha^{\omega*}_{\beta\delta} = \frac{i}{2}a_y(\alpha^{\omega*}_{xz}-\alpha^{\omega*}_{zx}), \quad (40)$$
$$\frac{i}{2}a_z\varepsilon_{\beta z\delta}\alpha^{\omega*}_{\beta\delta} = \frac{i}{2}a_z(\alpha^{\omega*}_{yx}-\alpha^{\omega*}_{xy}). \quad (41)$$

It is now clear that the origin invariance of αG demands a symmetric $\boldsymbol{\alpha}^{\omega}$ tensor. Such restriction would seem to prevent us from adopting the HT expansion of the electronic transition moments since the resulting polarizabilities are not symmetric. In fact, origin invariant resonance ROA intensities can be achieved even when HT effects are included in the calculation of the polarizabilities (see Sec. II B 4). The equation describing the origin dependence of the $\alpha\mathcal{G}$ invariant is very similar to Eq. (37) and imposes the same restriction on $\boldsymbol{\alpha}^{\omega}$,

$$\big(\mathcal{G}_{\beta\beta}(\boldsymbol{O}+\boldsymbol{a})\big)^{S*} = \left[\big(\mathcal{G}_{\beta\beta}(\boldsymbol{O})\big)^{S} + \frac{ia_\gamma}{2}\varepsilon_{\beta\gamma\delta}\alpha^{\omega}_{\delta\beta}\right]^{*}. \quad (42)$$

3. The $\beta_S(G)^2$ invariant

The symmetric anisotropic invariant of the mixed electric-magnetic dipole polarizability is composed of two parts: (i) $(\alpha_{\alpha\alpha})^S(G_{\beta\beta})^{S*}$, see Sec. II B 2, and (ii) $(\alpha_{\alpha\beta})^S(G_{\alpha\beta})^{S*}$ that under an origin shift transforms as

$$\big(\alpha_{\alpha\beta}\big)^S\big(G_{\alpha\beta}(\boldsymbol{O}+\boldsymbol{a})\big)^{S*} = \big(\alpha_{\alpha\beta}\big)^S\big(G_{\alpha\beta}(\boldsymbol{O})\big)^{S*} + \frac{ia_\gamma}{4}\big(\alpha_{\alpha\beta}\big)^S(\varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\alpha\delta}+\varepsilon_{\alpha\gamma\delta}\alpha^{\omega*}_{\beta\delta}). \quad (43)$$

Starting our analysis with the x-component of vector $\boldsymbol{a}$, after summing over α, β, and δ, we have

$$\frac{ia_x}{8}(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})(\varepsilon_{\beta x\delta}\alpha^{\omega*}_{\alpha\delta}+\varepsilon_{\alpha x\delta}\alpha^{\omega*}_{\beta\delta}) = \frac{ia_x}{4}\Big[-(\alpha_{xy}+\alpha_{yx})\alpha^{\omega*}_{xz}+(\alpha_{xz}+\alpha_{zx})\alpha^{\omega*}_{xy} - 2\alpha_{yy}\alpha^{\omega*}_{yz}+2\alpha_{zz}\alpha^{\omega*}_{zy}+(\alpha_{yz}+\alpha_{zy})(\alpha^{\omega*}_{yy}-\alpha^{\omega*}_{zz})\Big]. \quad (44)$$

In this case, Eq. (44) cannot be zero, but if $\boldsymbol{\alpha}$ is symmetric and $\boldsymbol{\alpha}^{\omega} = \omega_{rg,0}\boldsymbol{\alpha}$, its right-hand side becomes a pure real number,

$$\frac{ia_x}{8}(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})(\varepsilon_{\beta x\delta}\alpha^{\omega*}_{\alpha\delta}+\varepsilon_{\alpha x\delta}\alpha^{\omega*}_{\beta\delta}) = \frac{\omega_{rg,0}a_x}{2}\Big[i(\alpha_{xz}\alpha^{*}_{xy}-\alpha_{xy}\alpha^{*}_{xz}) + i(\alpha_{yz}\alpha^{*}_{yy}-\alpha_{yy}\alpha^{*}_{yz})+i(\alpha_{zz}\alpha^{*}_{yz}-\alpha_{yz}\alpha^{*}_{zz})\Big]. \quad (45)$$

The three terms between parentheses on the right-hand side of Eq. (45) are a product of complex numbers of the type $z_3 = i(z_1z_2^*-z_2z_1^*)$, i.e., pure real numbers. Similar equations hold for the a_y and a_z components. Therefore, the $\beta_S(G)^2$ invariant is origin independent only within the FC approximation. In addition, for simultaneous resonance with two or more non-degenerate electronic states, the equality $\boldsymbol{\alpha}^{\omega} = \omega_{rg,0}\boldsymbol{\alpha}$ is lost and the imaginary parts of terms like $\alpha_{xz}\alpha^{\omega*}_{xy}$ and $-\alpha_{xy}\alpha^{\omega*}_{xz}$ do not cancel each other exactly. Nevertheless, when the velocity representation is adopted, this origin dependence can be removed by adopting the same $\omega_{rg,0}$ in Eq. (36) and in the corresponding expressions for the ROA tensors. Such a cancellation scheme is exemplified in Sec. IV. The conditions for origin independence of the other invariants of $\boldsymbol{G}$ and $\boldsymbol{G}$ are similar and the corresponding equations are listed in Appendix A. The four rotational invariants involving tensors $\boldsymbol{A}$ and $\boldsymbol{A}$ require only $\boldsymbol{\alpha}$ to be symmetric and the equations showing their origin dependence are also given in Appendix A.

4. Origin invariance of the ROA cross sections

The intensity expressions for any possible CP-ROA experiment are built in terms of six rotational invariants (I_1, I_2, I_3, $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$), the angle ξ of the scattered beam relative to the incident beam, and the polarization states of either the incident or scattered beam if they are not modulated between right and left-CP states.[5] For instance, the cross section for the in-phase dual circular polarization scattering is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{ROA}}^{\mathrm{DCP_I}} = \frac{4K}{c}\left[I_1+\mathcal{I}_1+(I_2+\mathcal{I}_2)\cos\xi-\frac{1}{2}(I_3+\mathcal{I}_3)\sin^2\xi\right]. \tag{46}$$

The symbols I and $\mathcal{I}$ in this equation represent combinations of roman and script font ROA invariants, respectively,

$$I_1 = 45\alpha G + 7\beta_S(G)^2 + 5\beta_A(G)^2 + \beta_S(A)^2 - \beta_A(A)^2, \tag{47}$$

$$I_2 = 45\alpha G - 5\beta_S(G)^2 + 5\beta_A(G)^2 - 3\beta_S(A)^2 - \beta_A(A)^2, \tag{48}$$

$$I_3 = 45\alpha G + \beta_S(G)^2 - 5\beta_A(G)^2 + 3\beta_S(A)^2 - 3\beta_A(A)^2, \tag{49}$$

$$\mathcal{I}_1 = -45\alpha\mathcal{G} - 7\beta_S(\mathcal{G})^2 - 5\beta_A(\mathcal{G})^2 + \beta_S(\mathcal{A})^2 + \beta_A(\mathcal{A})^2, \tag{50}$$

$$\mathcal{I}_2 = -45\alpha\mathcal{G} + 5\beta_S(\mathcal{G})^2 - 5\beta_A(\mathcal{G})^2 - 3\beta_S(\mathcal{A})^2 + \beta_A(\mathcal{A})^2\,, \tag{51}$$

$$\mathcal{I}_3 = -45\alpha\mathcal{G} - \beta_S(\mathcal{G})^2 + 5\beta_A(\mathcal{G})^2 + 3\beta_S(\mathcal{A})^2 + 3\beta_A(\mathcal{A})^2. \tag{52}$$

As previously reported for (pure) electronic circular dichroism,[43] the rotatory strength tensor becomes origin independent when the electric dipole-electric quadrupole tensor and the electric dipole-magnetic dipole tensors are summed. Our equivalents here are the five invariants appearing in Eqs. (47)–(52). However, before summing the origin dependent terms related to $\boldsymbol{G}$ and $\boldsymbol{A}$ tensors (or $\boldsymbol{\mathcal{G}}$ and $\boldsymbol{\mathcal{A}}$), let us introduce the following approximations:

$$\alpha^{\omega}_{\alpha\beta} \approx \omega_{rg,0}\,\alpha_{\alpha\beta}, \tag{53}$$

$$\omega_0 \approx \omega_{rg,0}. \tag{54}$$

Equations (53) and (54) are good approximations for the resonance scattering when the $\omega_{rg,k}$'s can be neglected, i.e., when ground and excited state equilibrium geometries are similar. Furthermore, approximation (54) is used only when the electric quadrupole rotational invariants are computed; thus, it is employed in Eqs. (7) and (8) and their equivalents for the script font dipole-quadrupole tensors. The origin shifted I_1 invariant has 720 non-zero terms that can be organized as follows:

$$\begin{aligned}
I_1(\boldsymbol{O}+\boldsymbol{a}) = I_1(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ & ia_x\Big[-\frac{3}{2}(\alpha_{xx}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{xx})+\frac{3}{2}(\alpha_{xx}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{xx})-3(\alpha_{xy}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{xy})\\
&-\frac{3}{2}(\alpha_{xy}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{xy})+3(\alpha_{xz}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{xz})+\frac{3}{2}(\alpha_{xz}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{xz})\\
&-\frac{3}{2}(\alpha_{yx}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{yx})-6(\alpha_{yy}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{yy})+\frac{3}{2}(\alpha_{yz}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{yz})\\
&+6(\alpha_{yz}\alpha^*_{yy}-\alpha_{yy}\alpha^*_{yz})+\frac{3}{2}(\alpha_{zx}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{zx})-\frac{3}{2}(\alpha_{zy}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{zy})\\
&-6(\alpha_{zy}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{zy})+6(\alpha_{zz}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{zz})\Big]\\
&+ia_y\Big[+6(\alpha_{xx}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{xx})+\frac{3}{2}(\alpha_{xy}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{xy})-6(\alpha_{xz}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{xz})\\
&-\frac{3}{2}(\alpha_{xz}\alpha^*_{yy}-\alpha_{yy}\alpha^*_{xz})+3(\alpha_{yx}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{yx})+\frac{3}{2}(\alpha_{yx}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{yx})\\
&+\frac{3}{2}(\alpha_{yy}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{yy})-\frac{3}{2}(\alpha_{yy}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{yy})-\frac{3}{2}(\alpha_{yz}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{yz})\\
&-3(\alpha_{yz}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{yz})+\frac{3}{2}(\alpha_{zx}\alpha^*_{yy}-\alpha_{yy}\alpha^*_{zx})+6(\alpha_{zx}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{zx})\\
&-\frac{3}{2}(\alpha_{zy}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{zy})-6(\alpha_{zz}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{zz})\Big]\\
&+ia_z\Big[-6(\alpha_{xx}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{xx})+6(\alpha_{xy}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{xy})+\frac{3}{2}(\alpha_{xy}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{xy})\\
&-\frac{3}{2}(\alpha_{xz}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{xz})-6(\alpha_{yx}\alpha^*_{yy}-\alpha_{yy}\alpha^*_{yx})-\frac{3}{2}(\alpha_{yx}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{yx})\\
&+6(\alpha_{yy}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{yy})+\frac{3}{2}(\alpha_{yz}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{yz})-\frac{3}{2}(\alpha_{zx}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{zx})\\
&-3(\alpha_{zx}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{zx})+\frac{3}{2}(\alpha_{zy}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{zy})+3(\alpha_{zy}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{zy})\\
&-\frac{3}{2}(\alpha_{zz}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{zz})+\frac{3}{2}(\alpha_{zz}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{zz})\Big]\Big\}.
\end{aligned} \tag{55}$$

In the above equation, those pairs of terms related to the origin dependence of I_1 are all equal to zero since they have the general form: $\Im[i(z_1 z_2^* - z_2 z_1^*)]$, where z_1 and z_2 are complex numbers. Therefore, the origin invariance of I_1 does not require $\boldsymbol{\alpha}$ to be symmetric. Consequently, Herzberg-Teller calculations of resonance ROA may also be origin independent. However, it is worth to notice that a fully consistent HT calculation demands all three types of electronic transition moments $\boldsymbol{\mu}^{gr}$, $\boldsymbol{m}^{gr}$, and $\boldsymbol{\theta}^{gr}$ to be written in the form of Eq. (9). If only one (or two) type of transition moments is expanded into the normal coordinates, the resulting I_1 becomes origin dependent. To make this clear, one needs to remember that the ROA invariants of Eqs. (4)–(8) are obtained from the multiplication of the Raman polarizability by one of the four ROA tensors. In Eq. (55), all complex conjugated polarizabilities come from the origin dependence of the $\boldsymbol{G}$ and $\boldsymbol{A}$ tensors (Eqs. (19) and (24)) while the others are the Raman polarizabilities used to write the invariants of these tensors. Therefore, the two polarizabilities involved in the products $\alpha_{\alpha\beta}\alpha^*_{\gamma\delta}$ in Eq. (55) correspond to different levels, say, $\alpha^{L1}_{\alpha\beta}\alpha^{L2*}_{\gamma\delta}$, where $L1$ refers to the level used for $\boldsymbol{\mu}^{gr}$ (FC or HT) and $L2$ for $\boldsymbol{m}^{gr}$ (or $\boldsymbol{\theta}^{gr}$). As a consequence, $\Im[i(\alpha^{L1}_{\alpha\beta}\alpha^{L2*}_{\gamma\delta} - \alpha^{L1}_{\gamma\delta}\alpha^{L2*}_{\alpha\beta})] \neq 0$, thus resulting in origin dependent I_1. Proceeding in a similar way, one can show that the other five invariants may be origin independent as well, provided that the three transition moments are computed on the same footing, but the corresponding equations for the script font symbols ($\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$) are obtained when ω_R replaces ω_0 in Eq. (54). The effects of the origin shift on these five invariants are shown in Appendix B. In Sec. IV, the magnitude of the origin dependence of RROA intensities computed at the HT level will be analyzed by means of specific examples.

III. COMPUTATIONAL DETAILS

The electronic structure calculations were performed with a development version of the Gaussian suite of programs.[44] Ground and excited state properties were computed using the DFT and its time-dependent extension (TD-DFT) with the Becke 3-Parameter, Lee, Yang and Parr functional (B3LYP)[45] functional and the polarized Scuola Normale Superiore double-ζ (SNSD) basis set.[46,47] All Raman and ROA tensors were calculated using the *velocity representation* of the electric dipole and traceless electric quadrupole transition moments.[38] All vibronic polarizabilities were computed in a sum-over-state fashion, and the FC and HT integrals in Eq. (10) were evaluated by describing the potential energy surface (PES) of both ground and excited electronic states within the harmonic approximation. The data required to evaluate FC and HT integrals were obtained from the ground state geometry and its respective analytic Hessian, but for the excited state properties, two different approaches were used:[35] the Adiabatic Hessian (AH) model, where both PESs are treated at the same level, therefore an excited state geometry optimization and harmonic frequencies calculation are performed, and the Vertical Gradient (VG) model, where the excited state Hessian is assumed to be equal to the ground state one. The FC and HT integrals as well as the five types of polarizabilities required to obtain the resonance ROA spectrum were computed by extending to RROA the code developed by some of the present authors for resonance Raman and described in Ref. 31. The Raman and ROA intensities reported in this work are those from the backscattering SCP experiment with the sample being illuminated with unpolarized light.

IV. NUMERICAL RESULTS

In this section, we present some calculations performed for two test molecules, i.e., (S)-methyloxirane, (2R,3R)-dimethyloxirane, and (R)-4-F-2-azetidinone (Figure 1) in those regimes where some origin dependence is expected. The aim of this section is to provide numerical evidence of the extent of the origin dependence and to show the effectiveness of the strategies envisaged to remove this effect.

A. (S)-methyloxirane

The (S)-methyloxirane molecule (MOXY) has 24 normal modes of vibration and 18 of them are within the typical energy window of ROA experiments, i.e., below 2000 cm^{-1}. Its transition properties are listed in Table I, which contains singlet vertical excitation energies, oscillator strengths, and rotatory strengths obtained using several DFT functionals. According to Sec. II B, when the RROA tensors are evaluated at the FC level using a single excited state or a set of degenerate states, all RROA rotational invariants are origin independent and, by consequence, so is the RROA cross sections. On the other hand, for a set of non-degenerate states, origin invariance of $\beta_S(G)^2$ and $\beta_S(\mathcal{G})^2$ is not guaranteed, since $(\boldsymbol{\alpha}^{\omega})^p \neq \omega_{rg,0}\boldsymbol{\alpha}^p$ in this case. This condition for origin dependence

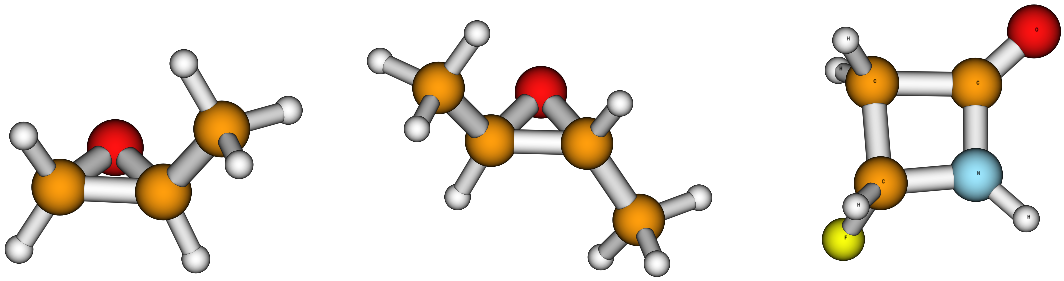

FIG. 1. Ball-and-stick representation of (S)-methyloxirane (left), (2R,3R)-dimethyloxirane (center), and (R)-4-F-2-azetidinone (right).

TABLE I. Singlet vertical excitation energies (ΔE, in nm), oscillator strengths ($f \times 10^3$), rotatory strengths in the velocity representation (R, in 10^{-40} esu^2 cm^2) of (S)-methyloxirane.

	B3LYP/SNSD[a]			B3LYP/SNSD[b]			M06/SNSD[a]			M06/SNSD[b]		
State	ΔE	f	R	ΔE	f	R	ΔE	f	R	ΔE	f	R
1	189	12.1	20.98	197	12.6	20.30	207	7.9	15.11	217	8.1	15.73
2	176	14.7	−14.22	182	13.5	−12.95	194	7.0	−3.66	203	6.4	−3.32
3	175	27.9	0.20	181	15.3	−9.74	193	19.1	−10.87	201	16.7	−9.98

[a]Computed at the ground state equilibrium geometry.
[b]Obtained at the equilibrium geometry of the S_1 state.

can be illustrated in the RROA scattering of MOXY involving the excited states S_1 and S_2, whose B3LYP/SNSD vertical excitation wavelengths are 189 nm and 176 nm. The RROA spectra at origin $\boldsymbol{O}$ and $\boldsymbol{O}+\boldsymbol{a}$ are shown in the top panels of Figure 2. They were calculated with an incident light beam $\lambda_0 = 189$ nm and the broadening factor $\Gamma = 500$ cm^{-1}. The origin shifted spectrum was generated through a molecular translation $\boldsymbol{T} = (50, -70, 90)$ Å and $\boldsymbol{T} = (500, -700, 900)$ Å, which is equivalent to have a shift vector $\boldsymbol{a} = -\boldsymbol{T}$. The resulting spectra show that the effect of the origin shift changes with the shift vector. In particular, in case a smaller shift is used (top-left panel of Figure 2), the spectra before and after the shifting are in qualitative agreement; however, at origin $\boldsymbol{O}+\boldsymbol{a}$, some bands lose intensity. The corresponding values of all RROA rotational invariants and cross section for the strongest band, the fundamental $\nu_{10} = 1150.5$ cm^{-1} (CH_2 wagging), are given in Table II. Similar tables are available for the other fundamental transitions as the supplementary material.[48] As expected, among the ten ROA invariants only $\beta_S(G)^2$ and $\beta_S(\mathcal{G})^2$ are affected by the origin change and, consequently, also the six linear combinations of invariants and cross section are affected. Much different results are obtained by using a larger shift vector (top-right panel of Figure 2). In fact, in this case not only peak intensities but also their sign changes, resulting in a totally different spectrum. This demonstrates that the origin dependence must be removed before setting

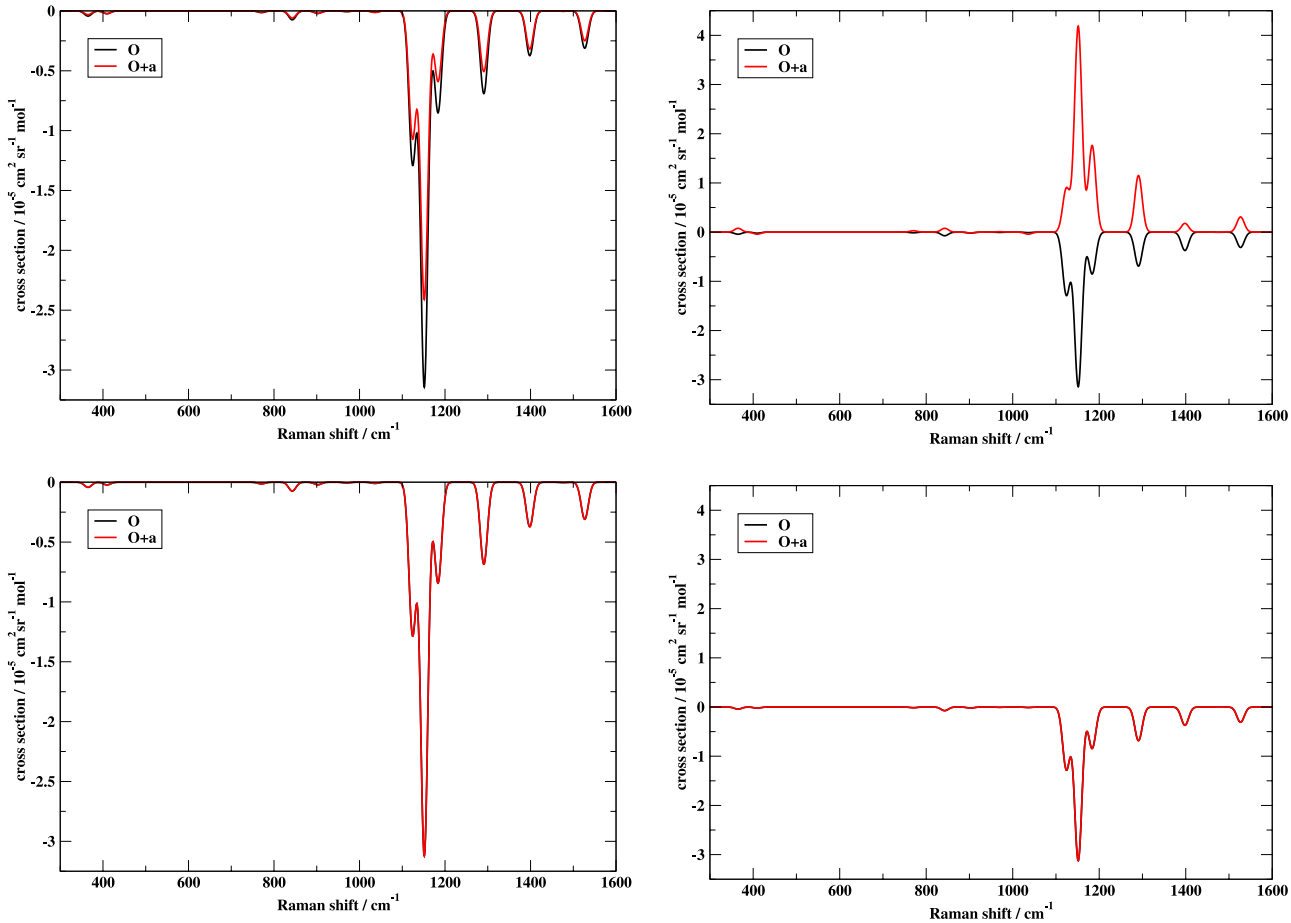

FIG. 2. B3LYP/SNSD RROA spectra of (S)-methyloxirane in vacuum obtained using S_1 and S_2 excited states, the VG and FC approximations, and $\lambda_0 = 189$ nm. The $\boldsymbol{O}$ + $\boldsymbol{a}$ spectra on the left panels were evaluated with $\boldsymbol{a} = (-50, 70, -90)$ Å and the corresponding spectra on the right panels with $\boldsymbol{a} = (-500, 700, -900)$ Å. The spectra in the bottom panels were calculated assuming that state S_2 has the same energy of S_1 in Eq. (28).

TABLE II. Origin dependence of the rotational invariants (in 10^{-3} Å^6) and ROA differential cross section (in 10^{-5} cm^2 sr^{-1} mol^{-1}) for the fundamental transition $\nu_{10} = 1151.5$ cm^{-1} of (S)-methyloxirane.

	VG-FC(S_1+S_2)[a]				AH-FCHT(S_1)[b]			
	$\boldsymbol{O}$	$\boldsymbol{O}+\boldsymbol{a}$[c]	$\boldsymbol{OI}$[d]	$\boldsymbol{OI}+\boldsymbol{a}$[e]	$\boldsymbol{O}$	$\boldsymbol{O}+\boldsymbol{a}$[f]	$\boldsymbol{OI}$[g]	$\boldsymbol{OI}+\boldsymbol{a}$
αG	−0.48	−0.48	−0.48	−0.48	−0.18	−5.83	−0.18	−5.83
$\alpha\mathcal{G}$	0.48	0.48	0.48	0.48	0.17	−5.48	0.17	−5.48
$\beta_S(G)^2$	−4.35	−3.34	−4.32	−4.32	−1.60	−14.08	−1.60	−14.08
$\beta_S(\mathcal{G})^2$	4.35	3.34	4.32	4.32	1.76	−10.70	1.76	−10.70
$\beta_A(G)^2$	0.00	0.00	0.00	0.00	0.12	38.00	0.12	38.00
$\beta_A(\mathcal{G})^2$	0.00	0.00	0.00	0.00	0.17	38.05	0.17	38.05
$\beta_S(A)^2$	0.06	0.05	0.06	0.06	0.03	37.41	0.03	37.41
$\beta_S(\mathcal{A})^2$	0.05	0.05	0.06	0.06	−0.10	−36.66	−0.11	−37.51
$\beta_A(A)^2$	0.00	0.00	0.00	0.00	−0.19	−114.80	−0.19	−114.80
$\beta_A(\mathcal{A})^2$	0.00	0.00	0.00	0.00	−0.23	−112.25	−0.23	−114.85
I_1	−52.14	−45.06	−51.63	−51.64	−18.71	−18.76	−18.71	−18.76
$\mathcal{I}_1$	−52.14	−45.06	−51.63	−51.64	−21.18	−17.75	−21.18	−21.20
I_2	−0.14	−5.21	−0.01	−0.00	0.44	0.49	0.44	0.49
$\mathcal{I}_2$	−0.14	−5.20	−0.00	−0.00	0.40	0.51	0.40	0.45
I_3	−25.92	−24.92	−25.57	−25.58	−9.83	−9.86	−9.83	−9.86
$\mathcal{I}_3$	−25.93	−24.92	−25.57	−25.58	−9.59	0.72	−9.62	−9.62
$d\sigma/d\Omega$	−3.13	−2.40	−3.11	−3.11	−1.10	−0.93	−1.10	−1.10

[a]B3LYP/SNSD ROA properties evaluated at the FC level using the VG model, two excited states, and $\lambda_0 = 189$ nm.
[b]B3LYP/SNSD ROA properties including HT effects, obtained using the AH model, a single excited state, and $\lambda_0 = 197$ nm.
[c]$\boldsymbol{a} = (-50, 70, -90)$ Å.
[d]Origin invariant results at origin $\boldsymbol{O}$.
[e]Origin invariant results at origin $\boldsymbol{O} + \boldsymbol{a}$.
[f]$\boldsymbol{a} = (-500, 700, -900)$ Å.
[g]Only I_1, I_2, I_3, $\mathcal{I}_1$, $\mathcal{I}_2$, $\mathcal{I}_3$, and $d\sigma/d\Omega$ are expected to be origin independent.

up theoretical models and computational strategies for RROA spectroscopy.

As mentioned in the theoretical section of this paper, the simplest strategy to remove origin dependence is to use the same excitation energy for both excited states. Nevertheless, the cause of origin dependence is the inequality $(\boldsymbol{\alpha}^\omega)^p \neq \omega_{rg,0}\boldsymbol{\alpha}^p$, which arises because $\omega_{rg,0}$ in the numerator of Eq. (32) changes as the counter $\{e_r\}$ spans non-degenerate excited states. This $\omega_{rg,0}$ frequency term comes from relation (17), and therefore, one can make the equality $(\boldsymbol{\alpha}^\omega)^p = \omega_{rg,0}\boldsymbol{\alpha}^p$ to hold by adopting the same $\omega_{rg,0}$ for the two excited states whenever Eq. (28) is used to convert the velocity electric dipole transition moment into the length representation. In addition, there is no need to change those $\omega_{rg,0}$ appearing in the denominator of the RROA tensors. The $\boldsymbol{O}$ and $\boldsymbol{O}+\boldsymbol{a}$ spectra incorporating this approximation are given in the bottom panels of Figure 2. In both cases, i.e., also in the case of the large shift vector causing sign inversion, the corrected spectra, which were obtained by assuming $c/(2\pi\omega_{rg,0}) = 189$ nm for both S_1 and S_2, are completely origin independent. As a consequence, also the corresponding RROA rotational invariants of the fundamental transition ν_{10} (see Table II) are all origin independent within the precision of 10^{-4} Å^6.

According to Sec. II B 4 and Appendix B, RROA cross sections evaluated by taking into account HT effects can display some origin dependence, even when the Raman and ROA polarizabilities are calculated using a single excited state. However, if the energy of the electronic transition is close to the energy of the incident and scattered radiation, $\hbar\omega_0 \approx \hbar\omega_{rg,0}$ and $\hbar\omega_R \approx \hbar\omega_{rg,0}$, such dependence is expected to be negligible. To illustrate this behavior, the RROA spectrum for the S_1 state only was calculated with $\lambda_0 = 197$ nm and $\Gamma = 500$ cm^{-1} using the AH model. This value for λ_0 corresponds to the $S_0 \rightarrow S_1$ vertical excitation wavelength at the equilibrium geometry of the S_1 state, where all transition moments and their derivatives were calculated. In our computational implementation of RROA with AH, this represents the most favorable condition for the cancellation of origin effects, because the frequency used in the conversion (Eq. (28)) is associated with ground and excited electronic states calculated at the excited state equilibrium geometry. Therefore, we have $\omega_0 = \omega_{rg,0}$ while $\omega_R \approx \omega_{rg,0}$ is a good approximation for low energy RROA transitions. Consequently, the I_1, I_2, and I_3 invariants are correctly origin invariant whereas there is no perfect cancellation for $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$. The SCP ROA intensities depend on both roman and script font invariants, as follows:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{ROA}} = \frac{4K}{c}(\mathcal{I}_1 + I_2\cos\xi - \mathcal{I}_3\sin^2\xi\sin^2\theta). \quad (56)$$

In Eq. (56), θ is related to the polarization conditions of the incident light. Therefore, the calculated spectra (top panel of Figure 3) exhibit some differences for high energy transitions. Notice that the reported origin shifted spectrum was obtained with $\boldsymbol{a} = (-500, 700, -900)$ Å, i.e., the shift showing huge effects in the FC calculation, see above. Moreover, in agreement with theory of Secs. II B 2 and II B 3, and Appendix A, in Table II we see that while all ROA invariants from αG to $\beta_A(\mathcal{A})^2$ are affected by the origin change, the origin dependence in the cross section is

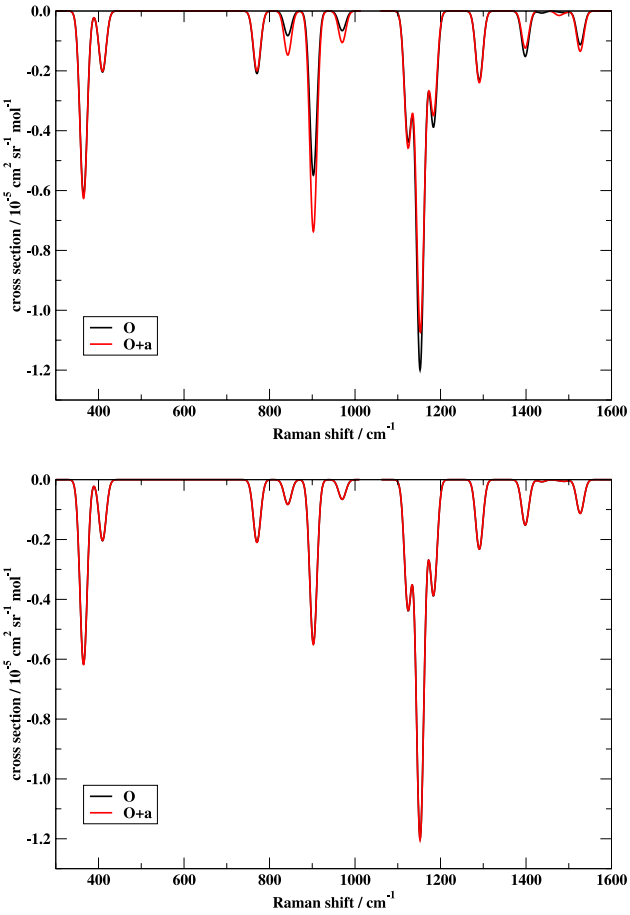

FIG. 3. Resonance ROA spectra for the S_1 state of (S)-methyloxirane in vacuum, computed at the B3LYP/SNSD level using the adiabatic Hessian and Herzberg-Teller approximations. Bottom spectra were obtained setting $\omega_0 = \omega_{rg,0}$ and $\omega_R = \omega_{rg,0}$ in the calculation of β_S and β_A invariants of $\boldsymbol{A}$ and $\boldsymbol{\mathcal{A}}$ tensors. The Raman excitation wavelength for these spectra is $\lambda_0 = 197$ nm, corresponding to the S_1 state, see Table I.

essentially caused by $\mathcal{I}_1$ and $\mathcal{I}_3$. For complete cancellation of origin effects, one needs $\omega_0 = \omega_{rg,0}$ in Eqs. (7) and (8) and $\omega_R = \omega_{rg,0}$ in their counterparts related to the $\boldsymbol{\mathcal{A}}$ tensor. As an approximation, one may intentionally evaluate β_S and β_A of $\boldsymbol{A}$ and $\boldsymbol{\mathcal{A}}$ tensors setting ω_0 and ω_R equal to $\omega_{rg,0}$ to obtain a RROA spectrum completely origin independent (bottom panel of Figure 3). This approximation will alter the values of $\beta_S(\mathcal{A})^2$ and $\beta_A(\mathcal{A})^2$ and remove the origin dependence of $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$, as it is shown in Table II. On the other hand, $\beta_S(A)^2$ and $\beta_A(A)^2$ remain unaltered because the frequency of incident light coincides with the frequency of the vertical electronic transition, i.e., $\omega_0 = \omega_{rg,0}$. Finally, one must stress that the velocity representation is more suitable for complete cancellation of origin effects in HT calculations as it does not require all $\omega_{rg,k}$ to be negligible.

Our results on the effect of origin dependence are confirmed by the data obtained by using a different functional. The origin dependence as a result of an origin shift of $\boldsymbol{a} = (-500, 700, -900)$ Å of RROA spectra calculated with the M06[49] functional is given as the supplementary material.[48] The origin effect is large, especially at the FC level; however, the sign of the bands is generally preserved except for a small band around 1050 cm^{-1}, which changes sign. The effect is less evident for HT calculations, and noticeably our strategy allows us to recover completely independent spectra also in this case.

B. (2R,3R)-dimethyloxirane

The disubstituted oxirane (2R,3R)-dimethyloxirane (DMOXY) was chosen to further illustrate origin dependence in FC and HT RROA spectra. This system has 33 normal vibrations and 25 with wavenumbers below 2000 cm^{-1}. Not surprisingly, the rotatory strengths of the first 2 excited states have opposite signs with respect to those of MOXY (Table III). Its FC RROA spectrum involving S_1 and S_2 states was calculated at the B3LYP/SNSD level using the VG model, $\Gamma = 500$ cm^{-1} and $\lambda_0 = 191$ nm. The vertical excitation wavelengths for these two states are 191 nm and 181 nm at the ground state equilibrium geometry. Differently from MOXY, the origin effects are so small for DMOXY that, even setting $\boldsymbol{a} = (-500, 700, -900)$ Å, there is no visible difference between the two spectra, shown in the top-left panel of Figure 4. Just to additionally check the proposed approximation to remove effects at the FC level, origin invariant spectra were calculated with $c/(2\pi\omega_{rg,0}) = 191$ nm for S_1 and S_2 in Eq. (28). The resulting spectra displayed in the bottom-left panel of Figure 4 are identical to the corresponding origin dependent pair.

The HT RROA spectrum for the S_1 state of DMOXY was calculated using the AH model, $\Gamma = 500$ cm^{-1} and $\lambda_0 = 199$ nm. This value of λ_0 corresponds to the vertical excitation wavenumber of state S_1 evaluated at the equilibrium geometry of this state (Table III). The shift vector for the $\boldsymbol{O} + \boldsymbol{a}$ spectrum is $\boldsymbol{a} = (-500, 700, -900)$ Å. These HT spectra, shown in the top-right panel of Figure 4, exhibit some origin dependence in the high energy region as expected. From Sec. II B, we know that this particular choice for λ_0 will cancel origin effects only in I_1 to I_3. Thus, in order to have origin independent cross sections, the quadrupole invariants $\beta_S(\mathcal{A})^2$ and $\beta_A(\mathcal{A})^2$ must be calculated with ω_R equal to $\omega_{rg,0}$, i.e., with $c/(2\pi\omega_R) = 189$ nm. The resulting spectra are shown in the bottom-right panel of Figure 4 and now are origin invariant in all Raman shift wavenumber range.

C. (R)-4-F-2-azetidinone

As a final example to illustrate origin effects in RROA spectrum, we consider the chiral 4-(R)-F-2-azetidinone molecule (R-AZE) shown in Figure 1, which is a β-lactam relevant for the synthesis of antibiotics.[50] R-AZE has a total of 24 normal modes and 20 vibrations with wavenumbers less than 2000 cm^{-1} at the B3LYP/SNSD level. Its transition properties are given in Table III for the first three excited states. The two-states FC RROA spectrum was calculated for the S_1 and S_2 states, whose vertical excitation wavenumbers are 215 and 192 nm, respectively, at the equilibrium ground state geometry. A pair of origin dependent FC spectra was generated with the shift vector $\boldsymbol{a} = (-500, 700, -900)$ Å (see the top-left panel of Figure 5). The parameters used in the RROA calculation were $\lambda_0 = 215$ nm and $\Gamma = 500$ cm^{-1}. The resulting spectra are clearly origin dependent, and in addition, they exhibit sign alternation as a consequence of the

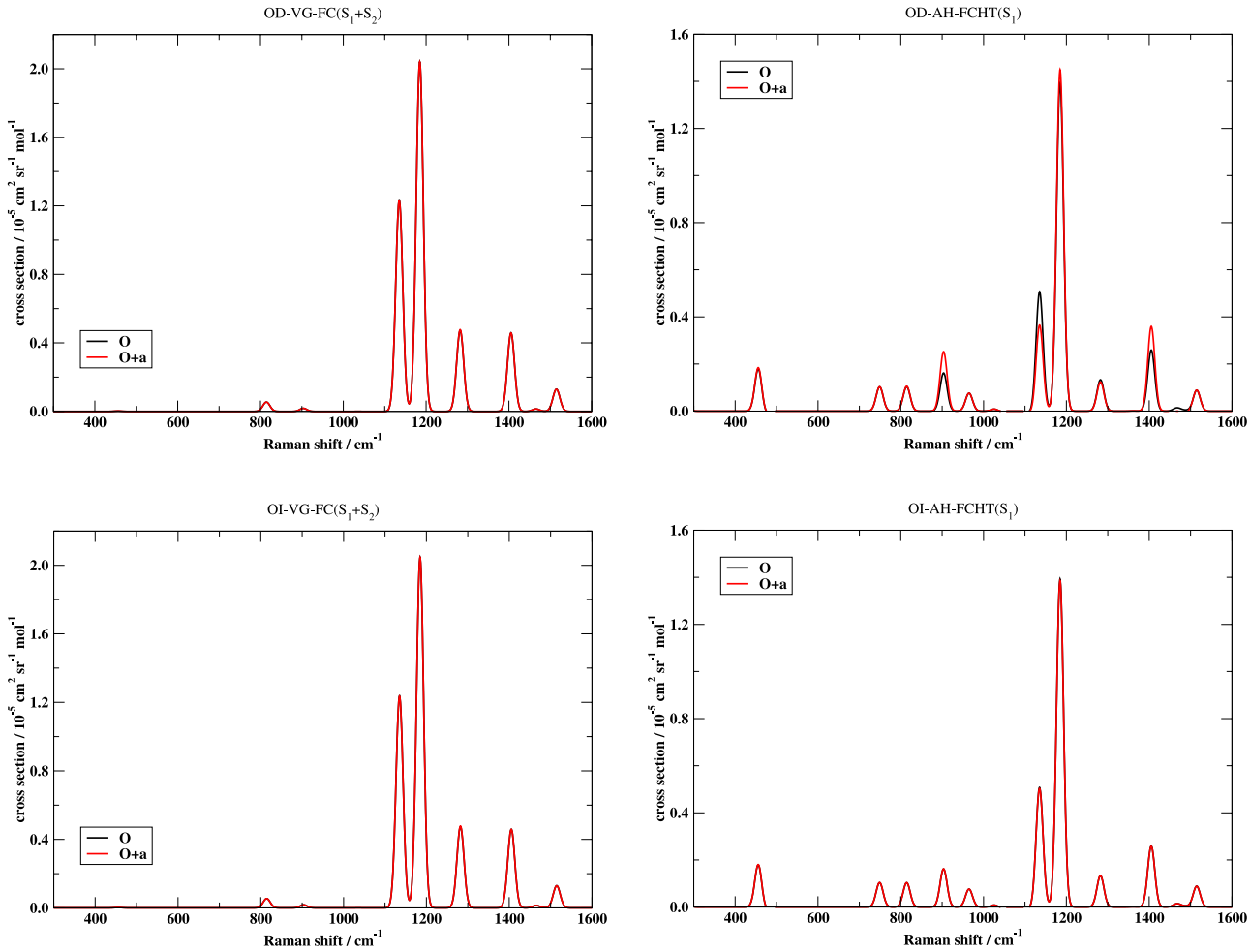

FIG. 4. B3LYP/SNSD resonance ROA spectra of **(2R,3R)-dimethyloxirane** in vacuum. Left spectra were calculated using two excited states and the vertical gradient and Franck-Condon models and an excitation wavelength $\lambda_0 = 191$ nm. Right spectra were obtained for a single excited state with the adiabatic Hessian and Herzberg-Teller models and $\lambda_0 = 199$ nm. The acronyms *OI* and *OD* mean origin invariant and origin dependent results, respectively.

opposite sign of the rotatory strength of the S_1 and S_2 states. Such a mechanism for sign alternation was already reported for the FC RROA spectrum of (S)-(+)-naproxen considering the first two excited electronic states.[27] As suggested for MOXY and DMOXY, if one chooses $c/(2\pi\omega_{rg,0}) = 215$ nm for both S_1 and S_2 in Eq. (28), the resulting RROA spectra become origin independent (see the bottom-left panel of Figure 5). The HT RROA spectrum of R-AZE was calculated for the S_2 state with $\lambda_0 = 209$ nm. This λ_0 coincides with the vertical excitation wavelength of the S_2 state (Table III); thus, I_1, I_2, and I_3 are origin invariant in this case. As before, $\Gamma = 500$ cm^{-1} and the excited state PES was modeled using the AH approach. The corresponding spectra are shown in the top-right panel of Figure 5, where the $\boldsymbol{O} + \boldsymbol{a}$ spectrum was obtained with $\boldsymbol{a} = (-500, 700, -900)$ Å. As expected, the origin dependence is strong for large wavenumbers, where the approximation $\omega_{rg,0} \approx \omega_R$ is poor. These spectra display a behavior not observed previously for MOXY and DMOXY, i.e., a sign alternation pattern at the HT level. The HT intensity borrowing mechanism is a different mechanism

TABLE III. Singlet vertical excitation energies (ΔE, in nm), oscillator strengths ($f \times 10^3$), rotatory strengths in the velocity representation (R, in 10^{-40} esu^2 cm^2) of (2R,3R)-dimethyloxirane and (R)-4-F-2-azetidinone.

	(2R,3R)-dimethyloxirane						(R)-4-F-2-azetidinone					
	B3LYP/SNSD[a]			B3LYP/SNSD[b]			B3LYP/SNSD[a]			B3LYP/SNSD[c]		
State	ΔE	f	R	ΔE	f	R	ΔE	f	R	ΔE	f	R
1	191	12.1	−14.68	199	11.2	−15.74	215	0.4	−6.50	228	0.3	−0.38
2	181	4.9	15.41	187	8.3	16.76	192	25.6	0.65	209	27.1	−6.57
3	179	8.9	−4.12	186	3.7	−5.25	180	11.2	−13.52	189	1.0	1.33

[a]Computed at the ground state equilibrium geometry.
[b]Obtained at the equilibrium geometry of the S_1 state.
[c]Obtained at the equilibrium geometry of the S_2 state.

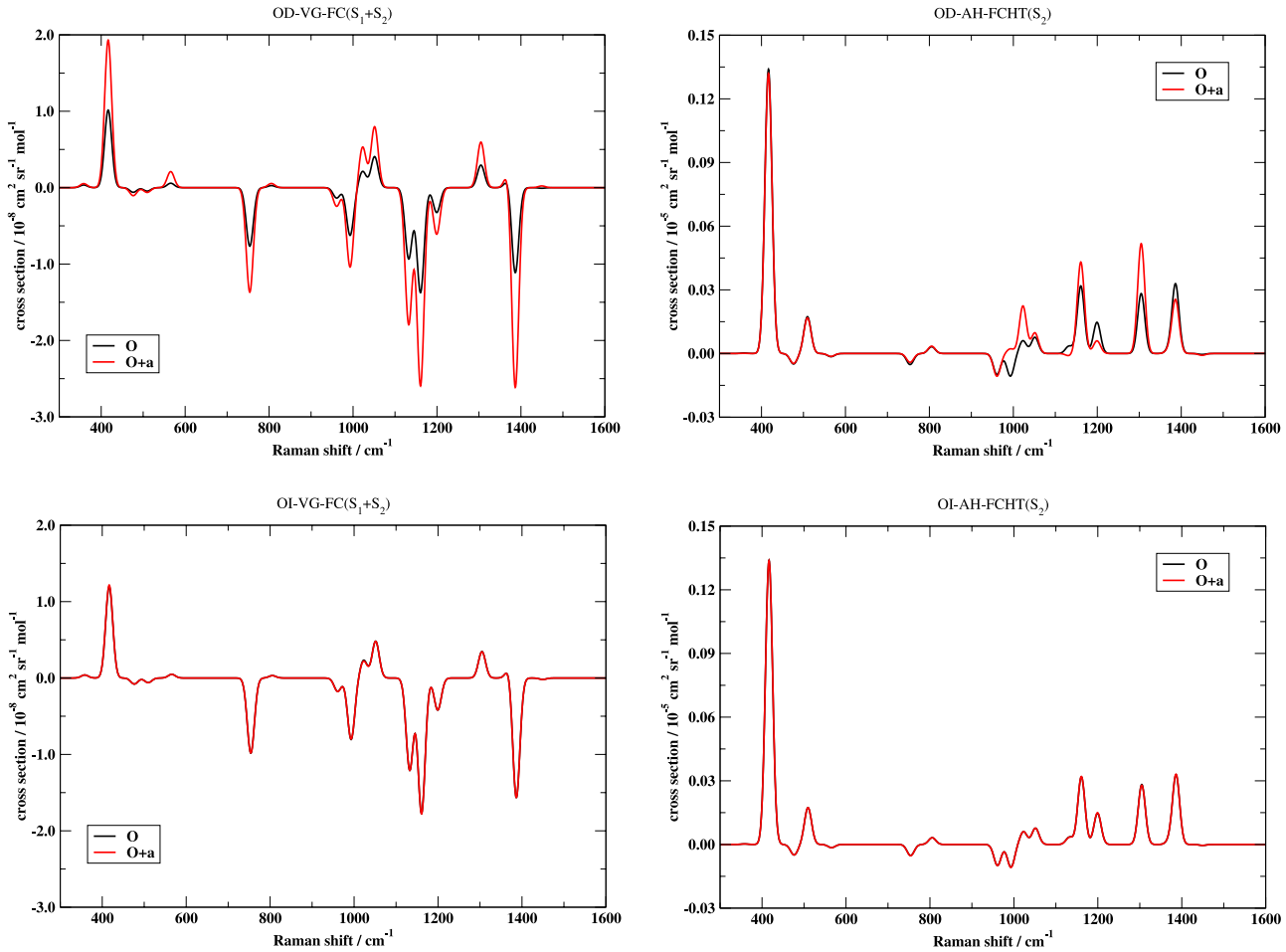

FIG. 5. B3LYP/SNSD resonance ROA spectra of **(R)-4-F-2-azetidinone** in vacuum. Left spectra were calculated using two excited states and the vertical gradient and Franck-Condon models and an excitation wavelength $\lambda_0 = 215$ nm. Right spectra were obtained for a single excited state with the adiabatic Hessian and Herzberg-Teller models and $\lambda_0 = 209$ nm. The acronyms *OI* and *OD* mean origin invariant and origin dependent results, respectively.

which introduces contributions from other excited states in the expression of the polarizability due to the coupling of the states involved in the scattering process with other close-lying electronic states.[35] Either the presence of several-excited-states or the HT mechanisms can give rise to RROA spectra with those characteristics observed in the far-from-resonance scattering, namely, sign change and bands that do not resemble the corresponding Raman bands. Following the same approach used in the previous examples, if $\beta_S(\mathcal{A})^2$ and $\beta_A(\mathcal{A})^2$ are calculated by imposing $\omega_R = \omega_{rg,0}$, i.e., fixed at 209 nm, the resulting spectra are origin invariant as it is shown in the bottom-right panel of Figure 5.

V. SUMMARY, CONCLUSIONS AND PERSPECTIVES

We have presented a theoretical and computational investigation on the origin dependence of the vibronic polarizabilities and rotational invariants defining RROA. Starting from the general time-independent theory of ROA, expressions for the origin dependence of the four ROA polarizability tensors were derived within the FC and HT approximations.

Our derivation shows that

- the isotropic rotational invariants αG and $\alpha\mathcal{G}$ of the roman font $\boldsymbol{G}$ and script font $\boldsymbol{\mathcal{G}}$ tensors are origin independent when $\boldsymbol{\alpha}^\omega$ is symmetric, i.e., at the FC level;
- the origin invariance of $\beta_S(G)^2$ and $\beta_S(\mathcal{G})^2$ requires $\boldsymbol{\alpha}^\omega$ symmetric and, in addition, that $\boldsymbol{\alpha}$, $\boldsymbol{G}$, and $\boldsymbol{\mathcal{G}}$ tensors are evaluated using a single excited state or a set of degenerate states;
- the anisotropic invariants of the electric dipole-quadrupole tensors $\beta_S(A)^2$ and $\beta_S(\mathcal{A})^2$ are origin invariant when $\boldsymbol{\alpha}$ is symmetric, i.e., at the FC level;
- the anti-symmetric anisotropic invariants $\beta_A(G)^2$, $\beta_A(\mathcal{G})^2$, $\beta_A(A)^2$, and $\beta_A(\mathcal{A})^2$ are zero in FC calculations and origin dependent at the HT level;
- for the linear combinations I_1, I_2, and I_3 of roman font ROA invariants to be origin independent, two conditions must be satisfied: (i) $\boldsymbol{\alpha}^\omega = \omega_{rg,0}\,\boldsymbol{\alpha}$, which holds exactly for single (or multiple degenerate) excited state scattering at FC level, in both length and velocity representations, and at the HT level in velocity representation, and (ii) $\omega_0 = \omega_{rg,0}$, i.e., the Raman excitation energy must be equal to the energy of the electronic transition;
- similarly, in order to the linear combinations $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$ of script font ROA invariants to be perfectly origin independent, one needs (i) $\boldsymbol{\alpha}^\omega = \omega_{rg,0}\,\boldsymbol{\alpha}$ and

(ii) $\omega_R = \omega_{rg,0}$, i.e., the scattered radiation with energy equal to the electronic transition;
- finally, the RROA cross sections are origin invariant when I_1, I_2, I_3, $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$ are origin invariant. At the HT level, the last three ($\mathcal{I}_1 - \mathcal{I}_3$) can be made exactly origin independent if $\beta_S(\mathcal{G})^2$ and $\beta_A(\mathcal{G})^2$ are evaluated with $\omega_{rg,0}$ replacing ω_R in their expressions.

Numerical tests performed for (S)-methyloxirane, (2R,3R)-dimethyloxirane, and (R)-4-F-2-azetidinone have shown that the calculated spectrum may be sensitive to the origin chosen; however, the strategy which is proposed to eliminate origin dependence in all cases is very effective. We note in this respect that different strategies, such as the one proposed for the optical rotation tensor by Pelloni and Lazzeretti[51] and which involves the definition of a reference system in terms of the principal axes of the polarizability expressed in the velocity gauge, are not successful in our case. This is primary due to the difficulty in the definition of a proper principal axes system for diagonalizing the tensor in Eq. (32): however, even if such a system could be defined, it does not suffice to cancel the origin dependence of RROA invariants.

The analysis we have reported, and the envisaged solutions to eliminate the dependence on the origin, paves the way to the development of effective time-independent strategies for the calculation of RROA spectra of molecular systems with the inclusion of Franck-Condon and Herzberg-Teller effects. Raman optical activity has been proven to be a valuable spectroscopic tool for the study of medium-large biomolecules in their natural environment, and hopefully, the availability of rigorous yet reliable computational approaches for ROA in the resonance regime should widen the applicability of such a technique. However, a reliable modeling should also focus on the computational applicability and scaling of the method with respect to system size. Also, in order to obtain reliable results for real systems, the inclusion of the effects due to the external environment (solvent/polymeric-protein matrix, etc.) appears to be mandatory, through the development of continuum or mixed explicit/continuum approaches. Finally, in order to increase the accuracy of the calculated spectra, the inclusion of anharmonic effects is substantial, possibly by exploiting reduced-dimensionality approaches in order to further enlarge the range of applications.

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APPENDIX A: ORIGIN DEPENDENCE OF $\beta_A(G)^2$, $\beta_A(\mathcal{G})^2$, $\beta_S(A)^2$, $\beta_S(\mathcal{A})^2$, $\beta_A(A)^2$ AND $\beta_A(\mathcal{A})^2$ INVARIANTS

In this appendix, we provide equations describing the origin dependence of the above six ROA invariants built from resonance Raman and ROA tensors written using the length representation.

1. The $\beta_S(\mathcal{G})^2$ invariant

The symmetric anisotropic invariant of the mixed magnetic-electric dipole polarizability has two parts: (i) $(\alpha_{\alpha\alpha})^S(\mathcal{G}_{\beta\beta})^{S*}$, which was considered in Sec. II B 2, and (ii) $(\alpha_{\alpha\beta})^S(\mathcal{G}_{\alpha\beta})^{S*}$, which under an origin shift transforms as following:

$$\begin{aligned}\frac{ia_\gamma}{8}(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})(\varepsilon_{\alpha\gamma\delta}\alpha^{\omega*}_{\delta\beta}+\varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\delta\alpha}) = {}& \frac{ia_x}{4}\Big[-(\alpha_{xy}+\alpha_{yx})\alpha^{\omega*}_{zx}+(\alpha_{xz}+\alpha_{zx})\alpha^{\omega*}_{yx}-2\alpha_{yy}\alpha^{\omega*}_{zy}+2\alpha_{zz}\alpha^{\omega*}_{yz}\\ &+(\alpha_{yz}+\alpha_{zy})(\alpha^{\omega*}_{yy}-\alpha^{\omega*}_{zz})\Big]+\frac{ia_y}{4}\Big[+(\alpha_{xy}+\alpha_{yx})\alpha^{\omega*}_{zy}-(\alpha_{yz}+\alpha_{zy})\alpha^{\omega*}_{xy}\\ &+2\alpha_{xx}\alpha^{\omega*}_{zx}-2\alpha_{zz}\alpha^{\omega*}_{xz}+(\alpha_{xz}+\alpha_{zx})(\alpha^{\omega*}_{zz}-\alpha^{\omega*}_{xx})\Big]\\ &+\frac{ia_z}{4}\Big[+(\alpha_{yz}+\alpha_{zy})\alpha^{\omega*}_{xz}-(\alpha_{xz}+\alpha_{zx})\alpha^{\omega*}_{yz}\\ &-2\alpha_{xx}\alpha^{\omega*}_{yx}+2\alpha_{yy}\alpha^{\omega*}_{xy}+(\alpha_{xy}+\alpha_{yx})(\alpha^{\omega*}_{xx}-\alpha^{\omega*}_{yy})\Big].\end{aligned} \tag{A1}$$

Analogously, for $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$ and $\boldsymbol{\alpha}^\omega = \omega_{rg,0}\boldsymbol{\alpha}$,

$$\begin{aligned}\frac{ia_\gamma}{8}(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})(\varepsilon_{\alpha\gamma\delta}\alpha^{\omega*}_{\delta\beta}+\varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\delta\alpha}) = {}& \frac{i\omega_{rg,0}a_x}{2}\Big[\alpha_{xz}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{xz}+\alpha_{yz}\alpha^*_{yy}-\alpha_{yy}\alpha^*_{yz}+\alpha_{zz}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{zz}\Big]\\ &+\frac{i\omega_{rg,0}a_y}{2}\Big[\alpha_{xx}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{xx}+\alpha_{xy}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{xy}+\alpha_{xz}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{xz}\Big]\\ &+\frac{i\omega_{rg,0}a_z}{2}\Big[\alpha_{xy}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{xy}+\alpha_{yy}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{yy}+\alpha_{yz}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{yz}\Big].\end{aligned} \tag{A2}$$

The right-hand side of Eq. (A2) is a real number and $\beta_S(\mathcal{G})^2$ is origin invariant

2. The $\beta_A(G)^2$ and $\beta_A(\mathcal{G})^2$ invariants

These anti-symmetric anisotropic invariants are obtained from the product of $(\alpha_{\alpha\beta})^A$ with the mixed electric-magnetic polarizabilities $\boldsymbol{G}$ and $\boldsymbol{\mathcal{G}}$. After shifting the origin from $\boldsymbol{O}$ to $\boldsymbol{O}+\boldsymbol{a}$, we obtain

$$\beta_A\big(G(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(G(\boldsymbol{O})\big)^2 + \frac{3a_\gamma}{16}\Im\Big[i(\alpha_{\alpha\beta}-\alpha_{\beta\alpha})(\varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\alpha\delta} - \varepsilon_{\alpha\gamma\delta}\alpha^{\omega*}_{\beta\delta})\Big], \tag{A3}$$

$$\beta_A\big(\mathcal{G}(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(\mathcal{G}(\boldsymbol{O})\big)^2 + \frac{3a_\gamma}{16}\Im\Big[i(\alpha_{\alpha\beta}-\alpha_{\beta\alpha})(\varepsilon_{\alpha\gamma\delta}\alpha^{\omega*}_{\delta\beta} - \varepsilon_{\beta\gamma\delta}\alpha^{\omega*}_{\delta\alpha})\Big]. \tag{A4}$$

In Sec. II B 3 and Appendix A 1, it was shown that the origin invariance of the symmetric anisotropic invariants requires $(\alpha_{\alpha\beta})^A = 0$. Here, again, this is the only way to cancel the second term on the right-hand side of Eqs. (A3) and (A4), as we can clearly see after performing the summation over the repeated greek indexes,

$$\begin{aligned}\beta_A\big(G(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(G(\boldsymbol{O})\big)^2 &+ \frac{3a_x}{8}\Im\Big[i(\alpha_{yx}-\alpha_{xy})\alpha^{\omega*}_{xz} + i(\alpha_{xz}-\alpha_{zx})\alpha^{\omega*}_{xy} + i(\alpha_{yz}-\alpha_{zy})(\alpha^{\omega*}_{yy}+\alpha^{\omega*}_{zz})\Big]\\ &+ \frac{3a_y}{8}\Im\Big[i(\alpha_{yx}-\alpha_{xy})\alpha^{\omega*}_{yz} + i(\alpha_{zy}-\alpha_{yz})\alpha^{\omega*}_{yx} + i(\alpha_{zx}-\alpha_{xz})(\alpha^{\omega*}_{xx}+\alpha^{\omega*}_{zz})\Big]\\ &+ \frac{3a_z}{8}\Im\Big[i(\alpha_{xz}-\alpha_{zx})\alpha^{\omega*}_{zy} + i(\alpha_{zy}-\alpha_{yz})\alpha^{\omega*}_{zx} + i(\alpha_{xy}-\alpha_{yx})(\alpha^{\omega*}_{xx}+\alpha^{\omega*}_{yy})\Big],\end{aligned} \tag{A5}$$

$$\begin{aligned}\beta_A\big(\mathcal{G}(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(\mathcal{G}(\boldsymbol{O})\big)^2 &+ \frac{3a_x}{8}\Im\Big[i(\alpha_{xy}-\alpha_{yx})\alpha^{\omega*}_{zx} + i(\alpha_{zx}-\alpha_{xz})\alpha^{\omega*}_{yx} + i(\alpha_{zy}-\alpha_{yz})(\alpha^{\omega*}_{yy}+\alpha^{\omega*}_{zz})\Big]\\ &+ \frac{3a_y}{8}\Im\Big[i(\alpha_{xy}-\alpha_{yx})\alpha^{\omega*}_{zy} + i(\alpha_{yz}-\alpha_{zy})\alpha^{\omega*}_{xy} + i(\alpha_{xz}-\alpha_{zx})(\alpha^{\omega*}_{xx}+\alpha^{\omega*}_{zz})\Big]\\ &+ \frac{3a_z}{8}\Im\Big[i(\alpha_{zx}-\alpha_{xz})\alpha^{\omega*}_{yz} + i(\alpha_{yz}-\alpha_{zy})\alpha^{\omega*}_{xz} + i(\alpha_{yx}-\alpha_{xy})(\alpha^{\omega*}_{xx}+\alpha^{\omega*}_{yy})\Big].\end{aligned} \tag{A6}$$

Evidently, such restriction will eliminate the contribution of $\beta_A(G)^2$ and $\beta_A(\mathcal{G})^2$ invariants to the ROA scattering.

a. The $\beta_S(A)^2$ and $\beta_S(\mathcal{A})^2$ invariants

The effect of an origin shift on the symmetric anisotropic invariants of the mixed electric dipole-quadrupole polarizabilities is shown as

$$\begin{aligned}\beta_S(A(\boldsymbol{O}+\boldsymbol{a}))^2 = \beta_S(A(\boldsymbol{O}))^2 &- \frac{3\omega_0}{16}\Im\Big\{i(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})\Big[\varepsilon_{\alpha\gamma\delta}\Big(a_\delta\alpha^*_{\gamma\beta} + a_\beta\alpha^*_{\gamma\delta} - \frac{2}{3}\delta_{\delta\beta}a_\eta\alpha^*_{\gamma\eta}\Big)\\ &+ \varepsilon_{\beta\gamma\delta}\Big(a_\delta\alpha^*_{\gamma\alpha} + a_\alpha\alpha^*_{\gamma\delta} - \frac{2}{3}\delta_{\delta\alpha}a_\eta\alpha^*_{\gamma\eta}\Big)\Big]\Big\},\end{aligned} \tag{A7}$$

$$\begin{aligned}\beta_S(\mathcal{A}(\boldsymbol{O}+\boldsymbol{a}))^2 = \beta_S(\mathcal{A}(\boldsymbol{O}))^2 &- \frac{3\omega_R}{16}\Im\Big\{i(\alpha_{\alpha\beta}+\alpha_{\beta\alpha})\Big[\varepsilon_{\alpha\gamma\delta}\Big(a_\delta\alpha^*_{\beta\gamma} + a_\beta\alpha^*_{\delta\gamma} - \frac{2}{3}\delta_{\delta\beta}a_\eta\alpha^*_{\eta\gamma}\Big)\\ &+ \varepsilon_{\beta\gamma\delta}\Big(a_\delta\alpha^*_{\alpha\gamma} + a_\alpha\alpha^*_{\delta\gamma} - \frac{2}{3}\delta_{\delta\alpha}a_\eta\alpha^*_{\eta\gamma}\Big)\Big]\Big\}.\end{aligned} \tag{A8}$$

The above formulae have five implicit summations over repeated greek indexes that result in 216 non-zero terms, for each invariant, that can be organized as follows:

$$\begin{aligned}\beta_S(A(\boldsymbol{O}+\boldsymbol{a}))^2 = \beta_S(A(\boldsymbol{O}))^2 &- \frac{3\omega_0}{8}\Im\Big\{ia_x\Big[2(\alpha_{xx}-\alpha_{zz})\alpha^*_{yz} + 2(\alpha_{yy}-\alpha_{xx})\alpha^*_{zy} + (\alpha_{yz}+\alpha_{zy})(\alpha^*_{zz}-\alpha^*_{yy})\\ &+ (\alpha_{xy}+\alpha_{yx})(2\alpha^*_{zx}-\alpha^*_{xz}) + (\alpha_{xz}+\alpha_{zx})(\alpha^*_{xy}-2\alpha^*_{yx})\Big] + ia_y\Big[2(\alpha_{yy}-\alpha_{xx})\alpha^*_{zx} + 2(\alpha_{zz}-\alpha_{yy})\alpha^*_{xz}\\ &+ (\alpha_{xz}+\alpha_{zx})(\alpha^*_{xx}-\alpha^*_{zz}) + (\alpha_{xy}+\alpha_{yx})(\alpha^*_{yz}-2\alpha^*_{zy}) + (\alpha_{yz}+\alpha_{zy})(2\alpha^*_{xy}-\alpha^*_{yx})\Big]\\ &+ ia_z\Big[2(\alpha_{xx}-\alpha_{zz})\alpha^*_{yx} + 2(\alpha_{zz}-\alpha_{yy})\alpha^*_{xy} + (\alpha_{xy}+\alpha_{yx})(\alpha^*_{yy}-\alpha^*_{xx}) + (\alpha_{xz}+\alpha_{zx})(2\alpha^*_{yz}-\alpha^*_{zy})\\ &+ (\alpha_{yz}+\alpha_{zy})(\alpha^*_{zx}-2\alpha^*_{xz})\Big]\Big\},\end{aligned} \tag{A9}$$

$$\beta_S(\mathcal{A}(\boldsymbol{O}+\boldsymbol{a}))^2 = \beta_S(\mathcal{A}(\boldsymbol{O}))^2 - \frac{3\omega_R}{8}\Im\Big\{ia_x\Big[2(\alpha_{xx}-\alpha_{zz})\alpha^*_{zy} + 2(\alpha_{yy}-\alpha_{xx})\alpha^*_{yz} + (\alpha_{yz}+\alpha_{zy})(\alpha^*_{zz}-\alpha^*_{yy}) + (\alpha_{xy}+\alpha_{yx})(2\alpha^*_{xz}-\alpha^*_{zx}) + (\alpha_{xz}+\alpha_{zx})(\alpha^*_{yx}-2\alpha^*_{xy})\Big] + ia_y\Big[2(\alpha_{zz}-\alpha_{yy})\alpha^*_{zx} + 2(\alpha_{yy}-\alpha_{xx})\alpha^*_{xz} + (\alpha_{xz}+\alpha_{zx})(\alpha^*_{xx}-\alpha^*_{zz}) + (\alpha_{xy}+\alpha_{yx})(\alpha^*_{zy}-2\alpha^*_{yz}) + (\alpha_{yz}+\alpha_{zy})(2\alpha^*_{yx}-\alpha^*_{xy})\Big] + ia_z\Big[+2(\alpha_{xx}-\alpha_{zz})\alpha^*_{xy} + 2(\alpha_{zz}-\alpha_{yy})\alpha^*_{yx} + (\alpha_{xy}+\alpha_{yx})(\alpha^*_{yy}-\alpha^*_{xx}) + (\alpha_{xz}+\alpha_{zx})(2\alpha^*_{zy}-\alpha^*_{yz}) + (\alpha_{yz}+\alpha_{zy})(\alpha^*_{xz}-2\alpha^*_{zx})\Big]\Big\}. \tag{A10}$$

Here, as we already observed for the invariants $\beta_S(G)^2$ and $\beta_S(\mathcal{G})^2$, the origin dependent term in Eqs. (A9) and (A10) cannot be zero but its imaginary part vanishes when $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$. Furthermore, since Eqs. (24) and (25) were obtained without identity (16), the restriction of $(\alpha_{\alpha\beta})^A = 0$ will remove the origin dependence of $\beta_S(A)^2$ and $\beta_S(\mathcal{A})^2$ even when multiple non-degenerate excited states are used to compute the ROA polarizabilities.

b. The $\beta_A(A)^2$ and $\beta_A(\mathcal{A})^2$ invariants

Under an origin shift, these two anti-symmetric anisotropic invariants behave as follows:

$$\beta_A\big(A(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(A(\boldsymbol{O})\big)^2 - \frac{3\omega_0}{16}\Im\Big\{i(\alpha_{\alpha\beta}-\alpha_{\beta\alpha})\Big[\varepsilon_{\alpha\gamma\delta}\big(a_\delta\alpha^*_{\gamma\beta} + a_\beta\alpha^*_{\gamma\delta} - \frac{2}{3}a_\eta\delta_{\delta\beta}\alpha^*_{\gamma\eta}\big) - \varepsilon_{\beta\gamma\delta}\big(a_\delta\alpha^*_{\gamma\alpha} + a_\alpha\alpha^*_{\gamma\delta} - \frac{2}{3}a_\eta\delta_{\delta\alpha}\alpha^*_{\gamma\eta}\big) + 2\varepsilon_{\alpha\beta\gamma}\big(a_\gamma\alpha^*_{\delta\delta} + a_\delta\alpha^*_{\delta\gamma} - \frac{2}{3}a_\eta\delta_{\gamma\delta}\alpha^*_{\delta\eta}\big)\Big]\Big\}, \tag{A11}$$

$$\beta_A\big(\mathcal{A}(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(\mathcal{A}(\boldsymbol{O})\big)^2 - \frac{3\omega_R}{16}\Im\Big\{i(\alpha_{\alpha\beta}-\alpha_{\beta\alpha})\Big[\varepsilon_{\alpha\gamma\delta}\big(a_\delta\alpha^*_{\beta\gamma} + a_\beta\alpha^*_{\delta\gamma} - \frac{2}{3}a_\eta\delta_{\delta\beta}\alpha_{\eta\gamma}\big) - \varepsilon_{\beta\gamma\delta}\big(a_\delta\alpha^*_{\alpha\gamma} + a_\alpha\alpha^*_{\delta\gamma} - \frac{2}{3}a_\eta\delta_{\delta\alpha}\alpha_{\eta\gamma}\big) + 2\varepsilon_{\alpha\beta\gamma}\big(a_\gamma\alpha^*_{\delta\delta} + a_\delta\alpha^*_{\gamma\delta} - \frac{2}{3}a_\eta\delta_{\gamma\delta}\alpha_{\eta\delta}\big)\Big]\Big\}. \tag{A12}$$

It is evident that the requirement of $(\boldsymbol{\alpha})^A = \mathbf{0}$, necessary for the origin invariance of $\beta_S(A)^2$ and $\beta_S(\mathcal{A})^2$, will turn $\beta_A(A)^2$ and $\beta_A(\mathcal{A})^2$ into zero. However, for completeness, we performed the summation over repeated greek indexes and organized the 324 non-zero terms of each invariant as follows:

$$\beta_A\big(A(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(A(\boldsymbol{O})\big)^2 - \frac{3\omega_0}{8}\Im\Big\{ia_x\Big[+(\alpha_{xy}-\alpha_{yx})(3\alpha^*_{xz}-2\alpha^*_{zx}) + (\alpha_{xz}-\alpha_{zx})(2\alpha^*_{yx}-3\alpha^*_{xy}) + (\alpha_{yz}-\alpha_{zy})(4\alpha^*_{xx}+3\alpha^*_{yy}+3\alpha^*_{zz})\Big] + ia_y\Big[+(\alpha_{xy}-\alpha_{yx})(3\alpha^*_{yz}-2\alpha^*_{zy}) + (\alpha_{yz}-\alpha_{zy}) \times(3\alpha^*_{yx}-2\alpha^*_{xy}) - (\alpha_{xz}-\alpha_{zx})(3\alpha^*_{xx}+4\alpha^*_{yy}+3\alpha^*_{zz})\Big] + ia_z\Big[+(\alpha_{xz}-\alpha_{zx})(2\alpha^*_{yz}-3\alpha^*_{zy}) + (\alpha_{yz}-\alpha_{zy})(3\alpha^*_{zx}-2\alpha^*_{xz}) + (\alpha_{xy}-\alpha_{yx})(3\alpha^*_{xx}+3\alpha^*_{yy}+4\alpha^*_{zz})\Big]\Big\}, \tag{A13}$$

$$\beta_A\big(\mathcal{A}(\boldsymbol{O}+\boldsymbol{a})\big)^2 = \beta_A\big(\mathcal{A}(\boldsymbol{O})\big)^2 - \frac{3\omega_R}{8}\Im\Big\{ia_x\Big[+(\alpha_{xy}-\alpha_{yx})(3\alpha^*_{zx}-2\alpha^*_{xz}) + (\alpha_{xz}-\alpha_{zx})(2\alpha^*_{xy}-3\alpha^*_{yx}) + (\alpha_{yz}-\alpha_{zy})(4\alpha^*_{xx}+3\alpha^*_{yy}+3\alpha^*_{zz})\Big] ia_y\Big[+(\alpha_{xy}-\alpha_{yx})(3\alpha^*_{zy}-2\alpha^*_{yz}) + (\alpha_{yz}-\alpha_{zy}) \times(3\alpha^*_{xy}-2\alpha^*_{yx}) + (\alpha_{zx}-\alpha_{xz})(3\alpha^*_{xx}+4\alpha^*_{yy}+3\alpha^*_{zz})\Big] ia_z\Big[+(\alpha_{zx}-\alpha_{xz})(3\alpha^*_{yz}-2\alpha^*_{zy}) + (\alpha_{yz}-\alpha_{zy})(3\alpha^*_{xz}-2\alpha^*_{zx}) + (\alpha_{xy}-\alpha_{yx})(3\alpha^*_{xx}+3\alpha^*_{yy}+4\alpha^*_{zz})\Big]\Big\}. \tag{A14}$$

APPENDIX B: ORIGIN DEPENDENCE OF THE SYMBOLS I_2, I_3, $\mathcal{I}_1$, $\mathcal{I}_2$, AND $\mathcal{I}_3$

Under the approximations that $\alpha^\omega_{\alpha\beta} \approx \omega_{rg,0}\,\alpha_{\alpha\beta}$ and $\omega_0 \approx \omega_{rg,0}$, the origin shifted I_2 and I_3 invariants have the form given as

$$I_2(\boldsymbol{O}+\boldsymbol{a}) = I_2(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ia_x\Big[-\frac{3}{2}(\alpha_{xx}\alpha^*_{yz}-\alpha_{yz}\alpha^*_{xx}) + \frac{3}{2}(\alpha_{xx}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{xx}) + \frac{3}{2}(\alpha_{xy}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{xy}) - \frac{3}{2}(\alpha_{xz}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{xz}) + \frac{3}{2}(\alpha_{yx}\alpha^*_{xz}-\alpha_{xz}\alpha^*_{yx}) + 3(\alpha_{yx}\alpha^*_{zx}-\alpha_{zx}\alpha^*_{yx}) + 6(\alpha_{yy}\alpha^*_{zy}-\alpha_{zy}\alpha^*_{yy}) + \frac{3}{2}(\alpha_{yz}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{yz}) + 6(\alpha_{yz}\alpha^*_{zz}-\alpha_{zz}\alpha^*_{yz}) - \frac{3}{2}(\alpha_{zx}\alpha^*_{xy}-\alpha_{xy}\alpha^*_{zx}) - 3(\alpha_{zx}\alpha^*_{yx}-\alpha_{yx}\alpha^*_{zx}) - \frac{3}{2}(\alpha_{zy}\alpha^*_{xx}-\alpha_{xx}\alpha^*_{zy})$$

$$
\begin{aligned}
&- 6(\alpha_{zy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zy}) - 6(\alpha_{zz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zz})\Big] \\
&+ ia_y\Big[- 6(\alpha_{xx}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xx}) - \frac{3}{2}(\alpha_{xy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xy}) - 3(\alpha_{xy}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xy}) \\
&- \frac{3}{2}(\alpha_{xz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xz}) - 6(\alpha_{xz}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xz}) - \frac{3}{2}(\alpha_{yx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yx}) \\
&+ \frac{3}{2}(\alpha_{yy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yy}) - \frac{3}{2}(\alpha_{yy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yy}) + \frac{3}{2}(\alpha_{yz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yz}) \\
&+ 6(\alpha_{zx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zx}) + \frac{3}{2}(\alpha_{zx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zx}) + 3(\alpha_{zy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zy}) \\
&+ \frac{3}{2}(\alpha_{zy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zy}) + 6(\alpha_{zz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zz})\Big] \\
&+ ia_z\Big[+ 6(\alpha_{xx}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xx}) + 6(\alpha_{xy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xy}) + \frac{3}{2}(\alpha_{xy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xy}) \\
&+ 3(\alpha_{xz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xz}) + \frac{3}{2}(\alpha_{xz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xz}) - 6(\alpha_{yx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yx}) \\
&- \frac{3}{2}(\alpha_{yx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yx}) - 6(\alpha_{yy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yy}) - 3(\alpha_{yz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yz}) \\
&- \frac{3}{2}(\alpha_{yz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yz}) + \frac{3}{2}(\alpha_{zx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zx}) - \frac{3}{2}(\alpha_{zy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zy}) \\
&- \frac{3}{2}(\alpha_{zz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zz}) + \frac{3}{2}(\alpha_{zz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zz})\Big]\Big\}, \qquad \text{(B1)}
\end{aligned}
$$

$$
\begin{aligned}
I_3(\boldsymbol{O}+\boldsymbol{a}) = I_3(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ & ia_x\Big[- \frac{9}{2}(\alpha_{xx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xx}) + \frac{9}{2}(\alpha_{xx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xx}) + 6(\alpha_{xy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{xy}) \\
&- \frac{9}{2}(\alpha_{xy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xy}) - 6(\alpha_{xz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{xz}) + \frac{9}{2}(\alpha_{xz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xz}) \\
&- \frac{9}{2}(\alpha_{yx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yx}) - 3(\alpha_{yy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{yy}) + \frac{9}{2}(\alpha_{yz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yz}) \\
&+ 3(\alpha_{yz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{yz}) + \frac{9}{2}(\alpha_{zx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zx}) - \frac{9}{2}(\alpha_{zy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zy}) \\
&- 3(\alpha_{zy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{zy}) + 3(\alpha_{zz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{zz})\Big] \\
&+ ia_y\Big[+ 3(\alpha_{xx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{xx}) + \frac{9}{2}(\alpha_{xy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xy}) - 3(\alpha_{xz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{xz}) \\
&- \frac{9}{2}(\alpha_{xz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xz}) - 6(\alpha_{yx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{yx}) + \frac{9}{2}(\alpha_{yx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yx}) \\
&+ \frac{9}{2}(\alpha_{yy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yy}) - \frac{9}{2}(\alpha_{yy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yy}) - \frac{9}{2}(\alpha_{yz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yz}) \\
&+ 6(\alpha_{yz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{yz}) + \frac{9}{2}(\alpha_{zx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zx}) + 3(\alpha_{zx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{zx}) \\
&- \frac{9}{2}(\alpha_{zy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zy}) - 3(\alpha_{zz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{zz})\Big] \\
&+ ia_z\Big[- 3(\alpha_{xx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{xx}) + 3(\alpha_{xy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{xy}) + \frac{9}{2}(\alpha_{xy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xy}) \\
&- \frac{9}{2}(\alpha_{xz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xz}) - 3(\alpha_{yx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{yx}) - \frac{9}{2}(\alpha_{yx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yx}) \\
&+ 3(\alpha_{yy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{yy}) + \frac{9}{2}(\alpha_{yz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yz}) - \frac{9}{2}(\alpha_{zx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zx}) \\
&+ 6(\alpha_{zx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{zx}) + \frac{9}{2}(\alpha_{zy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zy}) - 6(\alpha_{zy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{zy}) \\
&- \frac{9}{2}(\alpha_{zz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zz}) + \frac{9}{2}(\alpha_{zz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zz})\Big]\Big\}. \qquad \text{(B2)}
\end{aligned}
$$

For $\mathcal{I}_1$ to $\mathcal{I}_3$ script font invariants, assuming that $\alpha^{\omega}_{\alpha\beta} \approx \omega_{rg,0}\,\alpha_{\alpha\beta}$ and $\omega_R \approx \omega_{rg,0}$, one obtains

$$
\begin{aligned}
\mathcal{I}_1(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{I}_1(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ & ia_x\Big[+ \frac{3}{2}(\alpha_{xx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xx}) - \frac{3}{2}(\alpha_{xx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xx}) - \frac{3}{2}(\alpha_{xy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xy}) \\
&+ \frac{3}{2}(\alpha_{xz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xz}) - \frac{3}{2}(\alpha_{yx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yx}) - 3(\alpha_{yx}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yx})
\end{aligned}
$$

$$
\begin{aligned}
&- 6(\alpha_{yy}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yy}) - \frac{3}{2}(\alpha_{yz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yz}) - 6(\alpha_{yz}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yz})\\
&+ \frac{3}{2}(\alpha_{zx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zx}) + 3(\alpha_{zx}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zx}) + \frac{3}{2}(\alpha_{zy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zy})\\
&+ 6(\alpha_{zy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zy}) + 6(\alpha_{zz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zz})\Big]\\
&+ ia_y\Big[+ 6(\alpha_{xx}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xx}) + \frac{3}{2}(\alpha_{xy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xy}) + 3(\alpha_{xy}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xy})\\
&+ \frac{3}{2}(\alpha_{xz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xz}) + 6(\alpha_{xz}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xz}) + \frac{3}{2}(\alpha_{yx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yx})\\
&- \frac{3}{2}(\alpha_{yy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yy}) + \frac{3}{2}(\alpha_{yy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yy}) - \frac{3}{2}(\alpha_{yz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yz})\\
&- 6(\alpha_{zx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zx}) - \frac{3}{2}(\alpha_{zx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zx}) - 3(\alpha_{zy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zy})\\
&- \frac{3}{2}(\alpha_{zy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zy}) - 6(\alpha_{zz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zz})\Big]\\
&+ ia_z\Big[- 6(\alpha_{xx}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xx}) - 6(\alpha_{xy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xy}) - \frac{3}{2}(\alpha_{xy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xy})\\
&- 3(\alpha_{xz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xz}) - \frac{3}{2}(\alpha_{xz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xz}) + 6(\alpha_{yx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yx})\\
&+ \frac{3}{2}(\alpha_{yx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yx}) + 6(\alpha_{yy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yy}) + 3(\alpha_{yz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yz})\\
&+ \frac{3}{2}(\alpha_{yz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yz}) - \frac{3}{2}(\alpha_{zx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zx}) + \frac{3}{2}(\alpha_{zy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zy})\\
&+ \frac{3}{2}(\alpha_{zz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zz}) - \frac{3}{2}(\alpha_{zz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zz})\Big]\Big\},
\end{aligned}
\tag{B3}
$$

$$
\begin{aligned}
\mathcal{I}_2(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{I}_2(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ & ia_x\Big[+ \frac{3}{2}(\alpha_{xx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xx}) - \frac{3}{2}(\alpha_{xx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xx}) + 3(\alpha_{xy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{xy})\\
&+ \frac{3}{2}(\alpha_{xy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xy}) - 3(\alpha_{xz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{xz}) - \frac{3}{2}(\alpha_{xz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xz})\\
&+ \frac{3}{2}(\alpha_{yx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yx}) + 6(\alpha_{yy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{yy}) - \frac{3}{2}(\alpha_{yz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yz})\\
&- 6(\alpha_{yz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{yz}) - \frac{3}{2}(\alpha_{zx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zx}) + \frac{3}{2}(\alpha_{zy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zy})\\
&+ 6(\alpha_{zy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{zy}) - 6(\alpha_{zz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{zz})\Big]\\
&+ ia_y\Big[- 6(\alpha_{xx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{xx}) - \frac{3}{2}(\alpha_{xy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xy}) + 6(\alpha_{xz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{xz})\\
&+ \frac{3}{2}(\alpha_{xz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xz}) - 3(\alpha_{yx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{yx}) - \frac{3}{2}(\alpha_{yx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yx})\\
&- \frac{3}{2}(\alpha_{yy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yy}) + \frac{3}{2}(\alpha_{yy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yy}) + \frac{3}{2}(\alpha_{yz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yz})\\
&+ 3(\alpha_{yz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{yz}) - \frac{3}{2}(\alpha_{zx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zx}) - 6(\alpha_{zx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{zx})\\
&+ \frac{3}{2}(\alpha_{zy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zy}) + 6(\alpha_{zz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{zz})\Big]\\
&+ ia_z\Big[+ 6(\alpha_{xx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{xx}) - 6(\alpha_{xy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{xy}) - \frac{3}{2}(\alpha_{xy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xy})\\
&+ \frac{3}{2}(\alpha_{xz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xz}) + 6(\alpha_{yx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{yx}) + \frac{3}{2}(\alpha_{yx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yx})\\
&- 6(\alpha_{yy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{yy}) - \frac{3}{2}(\alpha_{yz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yz}) + \frac{3}{2}(\alpha_{zx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zx})\\
&+ 3(\alpha_{zx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{zx}) - \frac{3}{2}(\alpha_{zy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zy}) - 3(\alpha_{zy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{zy})\\
&+ \frac{3}{2}(\alpha_{zz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zz}) - \frac{3}{2}(\alpha_{zz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zz})\Big]\Big\},
\end{aligned}
\tag{B4}
$$

$$
\begin{aligned}
\mathcal{I}_3(\boldsymbol{O}+\boldsymbol{a}) = \mathcal{I}_3(\boldsymbol{O}) + \omega_{rg,0}\Im\Big\{ & ia_x\Big[+ \frac{9}{2}(\alpha_{xx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xx}) - \frac{9}{2}(\alpha_{xx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xx}) - \frac{9}{2}(\alpha_{xy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xy}) \\
& + \frac{9}{2}(\alpha_{xz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xz}) - \frac{9}{2}(\alpha_{yx}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yx}) + 6(\alpha_{yx}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yx}) \\
& - 3(\alpha_{yy}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yy}) - \frac{9}{2}(\alpha_{yz}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yz}) - 3(\alpha_{yz}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yz}) \\
& + \frac{9}{2}(\alpha_{zx}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zx}) - 6(\alpha_{zx}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zx}) + \frac{9}{2}(\alpha_{zy}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zy}) \\
& + 3(\alpha_{zy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zy}) + 3(\alpha_{zz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zz})\Big] \\
& + ia_y\Big[+ 3(\alpha_{xx}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{xx}) + \frac{9}{2}(\alpha_{xy}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xy}) - 6(\alpha_{xy}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xy}) \\
& + \frac{9}{2}(\alpha_{xz}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xz}) + 3(\alpha_{xz}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xz}) + \frac{9}{2}(\alpha_{yx}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{yx}) \\
& - \frac{9}{2}(\alpha_{yy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yy}) + \frac{9}{2}(\alpha_{yy}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yy}) - \frac{9}{2}(\alpha_{yz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yz}) \\
& - 3(\alpha_{zx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{zx}) - \frac{9}{2}(\alpha_{zx}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{zx}) + 6(\alpha_{zy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zy}) \\
& - \frac{9}{2}(\alpha_{zy}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zy}) - 3(\alpha_{zz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zz})\Big] \\
& + ia_z\Big[- 3(\alpha_{xx}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{xx}) - 3(\alpha_{xy}\alpha^*_{yy} - \alpha_{yy}\alpha^*_{xy}) - \frac{9}{2}(\alpha_{xy}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{xy}) \\
& + 6(\alpha_{xz}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{xz}) - \frac{9}{2}(\alpha_{xz}\alpha^*_{zy} - \alpha_{zy}\alpha^*_{xz}) + 3(\alpha_{yx}\alpha^*_{xx} - \alpha_{xx}\alpha^*_{yx}) \\
& + \frac{9}{2}(\alpha_{yx}\alpha^*_{zz} - \alpha_{zz}\alpha^*_{yx}) + 3(\alpha_{yy}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{yy}) - 6(\alpha_{yz}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{yz}) \\
& + \frac{9}{2}(\alpha_{yz}\alpha^*_{zx} - \alpha_{zx}\alpha^*_{yz}) - \frac{9}{2}(\alpha_{zx}\alpha^*_{yz} - \alpha_{yz}\alpha^*_{zx}) + \frac{9}{2}(\alpha_{zy}\alpha^*_{xz} - \alpha_{xz}\alpha^*_{zy}) \\
& + \frac{9}{2}(\alpha_{zz}\alpha^*_{xy} - \alpha_{xy}\alpha^*_{zz}) - \frac{9}{2}(\alpha_{zz}\alpha^*_{yx} - \alpha_{yx}\alpha^*_{zz})\Big]\Big\}. \qquad \text{(B5)}
\end{aligned}
$$

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